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METALS, CERAMICS
AND MATERIALS
TID-4500 (16th Ed.) UC-25

ULTRASONIC EXTRUSION: REDUCTION IN VEHICLE AND PLASTICIZER REQUIREMENTS FOR NON-CLAY CERAMICS

by
William B. Tarpley
Kenneth H. Yocom
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AEROPROJECTS INCORPORATED
WEST CHESTER, PENNSYLVANIA

Contract No. AT (30-1)-1836
Task 2

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ABSTRACT

Earlier work on the ultrasonic extrusion of lead and aluminum has been extended to the cold extrusion of plasticized ceramic compositions, resulting in significant improvements in increased extrusion rate (more than 100-fold), decreased extrusion pressure (2 to 10 fold), and in extruded specimen properties. It has also been found possible to extrude materials which are normally nonextrudable because of their low plasticizer or water content. Fused, ground alumina could be ultrasonically extruded with 15% less water than the minimum content without ultrasonics, and only 40 to 60% of that used in normal commercial practice. Significant improvement in the strength of as-extruded shapes, as well as reduced shrinkage and deformation in drying and firing, resulted. Compositions normally using 3 w/o ammonium alginate as a plasticizer can be extruded with 0.2 w/o plastizer when ultrasonically activated. It has been postulated that the ultrasonic effects observed are derived from reduction of surface friction, shear thinning of the thixotropic systems, particle orientation, surface-film rupture, and wetting phenomena.

As-extruded specimen improvement was evidenced by a smoother surface and freedom from cracks, tearing, and peeling. When steel dies were used, abrasion of the die surface sometimes caused a superficially discolored surface in nonultrasonic extrusions. The comparable ultrasonic extrusions showed little or no discoloration as the ultrasonic power level was increased. Ultrasonically extruded specimens which were fired in the same kiln loading as their corresponding controls show small but consistent increases in fired density. Water absorption was approximately 75% of the control. The highest moduli of rupture in the fired specimens were found in the ultrasonic specimens even though these required only 25% of the extrusion pressure of the controls.

The apparatus configurations utilized in the earlier hot lead and aluminum extrusion investigations were readily extended and modified for work with ceramics. Further evolution of practical adaptation to commercial hydraulic and augur extruders has taken place incident to other programs. In the present work, the most effective activation site was found to be the extrusion die. Effective power levels for the specimen size and stiffness investigated appeared to be from 250-1500 watts with an indication that stiffer mixes could be benefited at higher power levels. Extrusion equipment of larger size and input power has been successfully operated on other materials. The effects were observed in the ultrasonic activation of dies to produce 3/8-in. rod, hexagonal rod, hollow hexagonal tubing, ribbon, and 1/16-in. diameter rod. Extrusion ratios from 13.6 to 500 appear to be practical.

Ultrasonic extrusion of plasticized powders appears to be generally applicable to the wide range of powders and plasticizers studied in this investigation. These include submicron zirconia, 100-μ tabular alumina, fused alumina, nonsintered alumina, Ajax P clay, chemically reactive magnesia, porcelain, and titania. The compositions were plasticized with alginates, starch-glycerin, and several polymers.

The apparent universality of these effects suggests their application to other materials of interest in nuclear engineering, such as the oxides and carbides of uranium and thorium, beryllia, graphite, and cermet mixtures including those incompatible with aqueous vehicles. With proper application, ultrasonic extrusion may become a practical means for fabrication of materials not previously successfully extruded and also, a possible means for better control in coextrusion.

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ULTRASONIC EXTRUSION: REDUCTION IN VEHICLE AND PLASTICIZER REQUIREMENTS FOR NON-CLAY CERAMICS

I. INTRODUCTION

Economical production of ceramic parts of constant cross section, even with relatively complicated geometry, can be attained by mixing ceramic compounds with plasticizers and lubricants to form a mass that can be extruded or pressed through a shaped die at reasonable pressure. Water is most commonly used as a plasticizer and lubricant for clays, but non-clay bodies require the addition of organic plasticizers such as starch, glycerine, waxes, etc. Metal and cermet powder mixtures may be extruded with binders dissolved in nonaqueous solvents, and carbon shapes are commonly extruded with resin or pitch binders.

Of these additives, only the binder, which holds the material together and retains shape through drying and into firing, serves any purpose after the extrusion is accomplished. Normally, all added materials are undesirable in the finished piece and should, therefore, disappear on firing.

In the usual case, water content is reduced by drying in order to form a body which, upon sintering, shrinks further and develops a density close to the theoretical, and develops, as well, considerable strength and uniformity. Although the extrusion of clay compositions has been studied to a considerable extent (1, 2)*, the extrusion of non-clay materials has been found somewhat more difficult because of their nonplastic properties (3) which lead to excessive pressure, die wear, poor die fill, and undesirable surface properties.

A number of workers in the field of ceramics (4, 5, 6) have reported that when it is possible to reduce the water content of ceramic compositions for various methods of processing, it is frequently observed that greater density and uniformity are associated with the lower shrinkage and higher strength of the compacts formed. Alternate ceramic forming processes such as slip casting, ramming, cold pressing, and hot pressing can sometimes be used with non-clay materials, but these processes frequently involve long processing times and cannot be applied to shapes of relatively great length-to-diameter ratio (7, 8). Hot extrusion (9, 10, 11) has been attempted but with certain difficulties.

In the processing of nuclear reactor fuel materials, uniformity, dimensional stability, retention of shape, maximum density after firing, and physical strength are the prime requirements. A smooth surface minimizes subsequent finishing by grinding which is often difficult. Ceramic extrusion

* Numbers in parentheses designate references listed at end of report.

techniques have been considered and/or investigated for various rod, tube and plate-shaped fuel elements. Urania rods were made experimentally (8) and similar processes are currently under investigation (12) to prepare specimens for in-pile studies. Extrusion has also been considered for the fabrication of urania or uranium carbide fuels in graphite matrices. The use of cermet mixtures has created new problems in development of forming methods, such as hot pressing, and attention is now being given to the cold extrusion of such materials.

It follows that any modification of extrusion conditions, which permits lower concentrations of added ingredients, may result in a higher value of desired properties in the finished shape. Early work in this laboratory on the application of ultrasonic energy to the hot extrusion of metals (13) and to the compaction of metallic powders (14) suggested that improvements in density, uniformity, and surface finish might be attained. In the extrusion of lead and aluminum, significant reductions in extrusion force (up to 20%) were achieved. Twofold to threefold increases in rate were observed at constant force. Ultrasonic activation was shown possible for both shear and conical dies, for heated containers, and for the ram. This work culminated in the ultrasonic extrusion cladding of tubular shapes through activation of a complex webbed die. Delivery of appreciable vibratory power into the desired region of such pressurized systems has been made possible through the development of force-insensitive mounting systems at this laboratory. Thus, a significant carry over of successful ultrasonic technology to apparatus for ceramic extrusion was possible. The mechanism of action of ultrasonic vibration on ceramic compositions appears to be somewhat different than in the case of metals, but findings on flow improvement (15, 16, 17, 18) suggested probability of success.

II. BACKGROUND

Extrusion pressure and rate appear to involve such factors as friction of the ceramic body at various equipment surfaces, viscous flow losses, thixotropy and, for complex shapes, bridging or die fill. Surface pickup, tearing, and fissures are particularly noticeable when stiff compositions are extruded.

In general, ceramic bodies can be plastically formed only over a rather critical range of water content. At water contents above the critical, objects do not retain their form; at water content below critical, required extrusion forces are frequently too high for existing equipment; peeling and other surface defects are often observed in the parts, and die fill is poor. Stress-strain diagrams obtained for ceramic pastes of varying water content (35-50%) have been described as "very much like those for a metal" (6), and the marked influence of water content on rheological properties has been delineated.

Plastic forming processes are generally believed to depend to a great extent on particle size and shape as well as particle size distribution of the initial material.

Clays are particularly suited to plastic forming processes because they are usually self-plasticizing, and only water additions are required. On the other hand, auxiliary binders must be added to non-clay ceramic formulations to obtain workable material. Selection of binders is usually a trial and error process and, as a result, work with a large number of binders has been reported (6, 19, 20, 21, 22). Binders used include such materials as flour, cellulose acetate, sodium silicate, starch-glycerol, and numerous alginates. These binders have been used for extrusion and other processing of non-clay ceramics, including alumina, beryllia, magnesia, thoria, urania, and zirconia. However, successful extrusions depend upon the proper balance between ceramic powder, plasticizer, mixing procedure and die design (3).

Binder selection has a marked effect on sintered properties as well as on green properties. Often, binders giving the best extrusion results show harmful effects on sintered properties. Furthermore, extreme purity requirements for certain applications, especially nuclear, may rule out otherwise excellent materials.

A. Ultrasonic Phenomena of Significance to Ceramic Extrusion

One of the readily noticeable effects of ultrasonic excitation is the reduction of friction at surfaces. Although the mechanism has not been precisely defined, many qualitative examples exist. The most obvious manifestation is the slippery feeling of activated systems.

Some early measurements conducted in this laboratory indicated that the force necessary to traverse a weighted sheet of cellulose acetate-butyrate plastic across a stainless steel bar was reduced to one-seventh its original value when the bar was activated at 20 kc/sec in a longitudinal mode. Similarly, the fitting of close-tolerance, generally tubular, metal parts could not be accomplished by ordinary means, but when elastically excited at ultrasonic frequency the metal parts were readily assembled at interference fits (23). These examples, most easily attributed to purely antifrictional effects, involved large objects. The increased rate of passage of metal powders through orifices and in the filling of cold pressed dies (14) and tubes (17) with metal or ceramic powders appears to involve reduction in both wall and interparticulate friction.

Increased flow of materials that can be directly activated by ultrasonic means has been observed in this laboratory. While studying the influence of ultrasonic vibration on the rheological properties of thixotropic carboxymethylcellulose suspensions in water, and thorium mercuride particle suspensions in mercury (15), evidence was found that the application of ultrasonic vibration produced over a fifty-fold increase in flow through a small orifice at a pressure head of 0.5 psig.

The shear-thinning effect on thixotropic systems is dramatic: stiff gels can be made to flow like thin liquids through an orifice under no force but their own weight, by ultrasonic excitation of the container and opening (15). Related effects of ultrasonics, such as surface film rupture and improved wetting, as well as particle orientation, may also contribute significantly.

These influences on the flow of various materials, ranging from dry powders to thick suspensions, indicate an excellent possibility of affecting the internal viscous flow characteristics of the ceramic body as it goes through the acceleration zone during extrusion.

B. Special Equipment Considerations

In the design of ultrasonic equipment for applications in which high forces are to be imposed on the system, or in which hermetic sealing is required, one of the major problems is the necessity to employ transducer-coupler mounting systems that are not force sensitive. With ordinary support methods, the imposition of an appreciable load on the system results in prohibitive power losses expended in vibrating the support structure, causes substantial shifts from the design frequency of the system, and markedly reduces the efficiency of ultrasonic energy transmission. For example, with certain ultrasonic drilling equipment, drilling rates decrease as the force between tool tip and workpiece exceeds a critical level, which is usually only a few pounds (24, 25, 26).

As a result of many years' experience with the problem of delivering high ultrasonic intensities into the zone of the system where it will do useful work, workers at this laboratory have developed unique, force-insensitive ultrasonic systems (27). With such mounting systems, actual measurements indicate little deviation from the design frequency of the transducer-coupler array over a wide range of applied force. For example, in cold pressing, a maximum deviation of about 2% with the application of forces up to 80 tons was observed.

Without such force-insensitive mounts, the activation of practical extrusion systems and a number of other apparatus arrays involving entry into environments normally considered forbidden to ultrasonic treatment would not have been possible. Ultrasonic welding, for example, is effective and practical because clamping forces can be imposed on the system without impairing its efficiency. Force-insensitive ultrasonic apparatus used in powder-metallurgical studies permitted the application of pressures in the order of 80 tons/in.^{2} during the introduction of vibratory motion both axially and laterally into powdered-metal compacts.

C. Ultrasonic Extrusion of Metals

More directly analogous to the problem at hand are the results we have obtained with the application of ultrasonic energy during extrusion of lead and aluminum (13, 28). This work demonstrated substantial increases in extrusion rates at constant extrusion forces and significant decreases in force levels at constant rates.

Initial studies, carried out with laboratory-type equipment utilizing a 100-ton hydraulic arbor press, involved direct extrusion of billets 1.25-in. diameter by 6-in. length through a circular die at an extrusion ratio of 25:1 for lead and 11:1 for aluminum. The extrusion array included provisions for separate ultrasonic activation of the die, the ram, and the container at nominal vibratory frequencies of 20 kc/sec. The two types of dies were used with axial excitation, one having a flat face and the other a conical face. Axial vibration was also applied through the ram. Flexural vibration of the container was achieved by means of a transducer attached normal to the container which was designed to resonate flexurally at the transducer frequency. To provide increased ultrasonic power, considered necessary for the extrusion of aluminum, a multi-transducer die-activation system was employed.

The results of these experiments showed that ultrasonic activation of a shear die reduced the force required for extrusion of lead (at a constant rate) by 16 to 28%. In the case of aluminum, initial extrusion forces were reduced by 15 to 18% compared to a nonultrasonic billet. The application of pulsed ultrasonic energy during aluminum extrusion produced reductions in the range of 10 to 25% in extrusion force when the shear die was activated.

Exploratory flow-pattern studies were made with a limited number of laminated billets composed of aluminum wafers with interlayered copper spheres. Cross sections of these billets indicated some evidence of less circuitous flow of the metal in the vicinity of the ram face in the ultrasonic billets, but no conclusive information was derived.

Laboratory apparatus was also used for very preliminary experimentation in the ultrasonic extrusion of generally tubular aluminum shapes with wall thickness in the 10-mil region. The transducer array could be driven with either an electronic generator or motor-alternator. With this apparatus, extrusion forces at constant rates were reduced from about 52 to 44 tons/in.^{2}, and extrusion rates (at a constant ram force of 44 tons/in.^{2}) were increased by 200 to 300%.

D. Rationale

The objects of this investigation are to extrude nonplastic ceramic mixtures containing reduced quantities of moisture and binder in order to improve material uniformity and other properties, to achieve improved surface, and to improve extrusion conditions by increasing rate, decreasing pressure, and reducing die wear.

Positive results in the reduction of sliding friction, in the promotion of flow of thixotropic pastes and of powders, and in the ultrasonic extrusion of both aluminum and lead at lower extrusion forces and with modified flow patterns in the acceleration zone, suggest a high probability of success in reducing both surface and internal friction in the extrusion of ceramic components. This, in turn, led to the assumption that drier and stiffer materials could be effectively extruded by means of ultrasonic activation. Reduced binder and moisture contents would be expected to reduce shrinkage and to improve density and dimensional integrity of the fired objects.

III. EQUIPMENT

The experimental ultrasonic extrusion apparatus for this investigation evolved from the arrays previously used in metal extrusion (13). Multiple magnetostrictive transducer assemblies were powered by RF current from either a simple 20-kc, 2-kw motor-alternator with a narrow-range frequency control, or from a more flexible wide-range, tunable, electronic power supply. Vibratory motion from the transducer assembly was transmitted through an acoustically designed coupler attached to the lower press platen by means of a rugged force-insensitive mount. The coupler terminated in the die configuration and formed a close fit with the container (Fig. 1). Die attachment was accomplished by brazing, and for interchangeable die designs, by machine-screw threads of fine pitch. Internal die contours followed recommended practice*. Ultrasonic container activation followed the procedure of the earlier metal studies (13).

Most of the ultrasonic extrusion of ceramics was carried out on a 25-ton Wilson hydraulic press, valved so that the maximum load was controlled and so that the ram speed could be varied. Figure 2 shows this press. The de-airing flange is shown in position for vacuum air removal. It is subsequently removed and replaced by the ultrasonic extrusion head as generally indicated in Fig. 1.

A total of four 1-3/8-in. ID extrusion containers were used with this press. A 7.5-in.-long, nonactive container was used initially and a 22-in. long, nonactive container was used during later stages of work. In addition, one 11.5-in.-long container and one 22-in.-long container were designed for ultrasonic activation at 20 kc. The first active container was designed to provide a bell mode, and the second active container, a flexural mode of vibration.

The maximum speed of ram travel limited the extrusion rates to 243 in./min with a 3/8-in. die, and 4400 in./min with a 1/16-in. die. The press was operated for vertical downward extrusion.

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* The services of Dr. John Koenig, Rutgers University, as ceramics consultant are gratefully acknowledged.

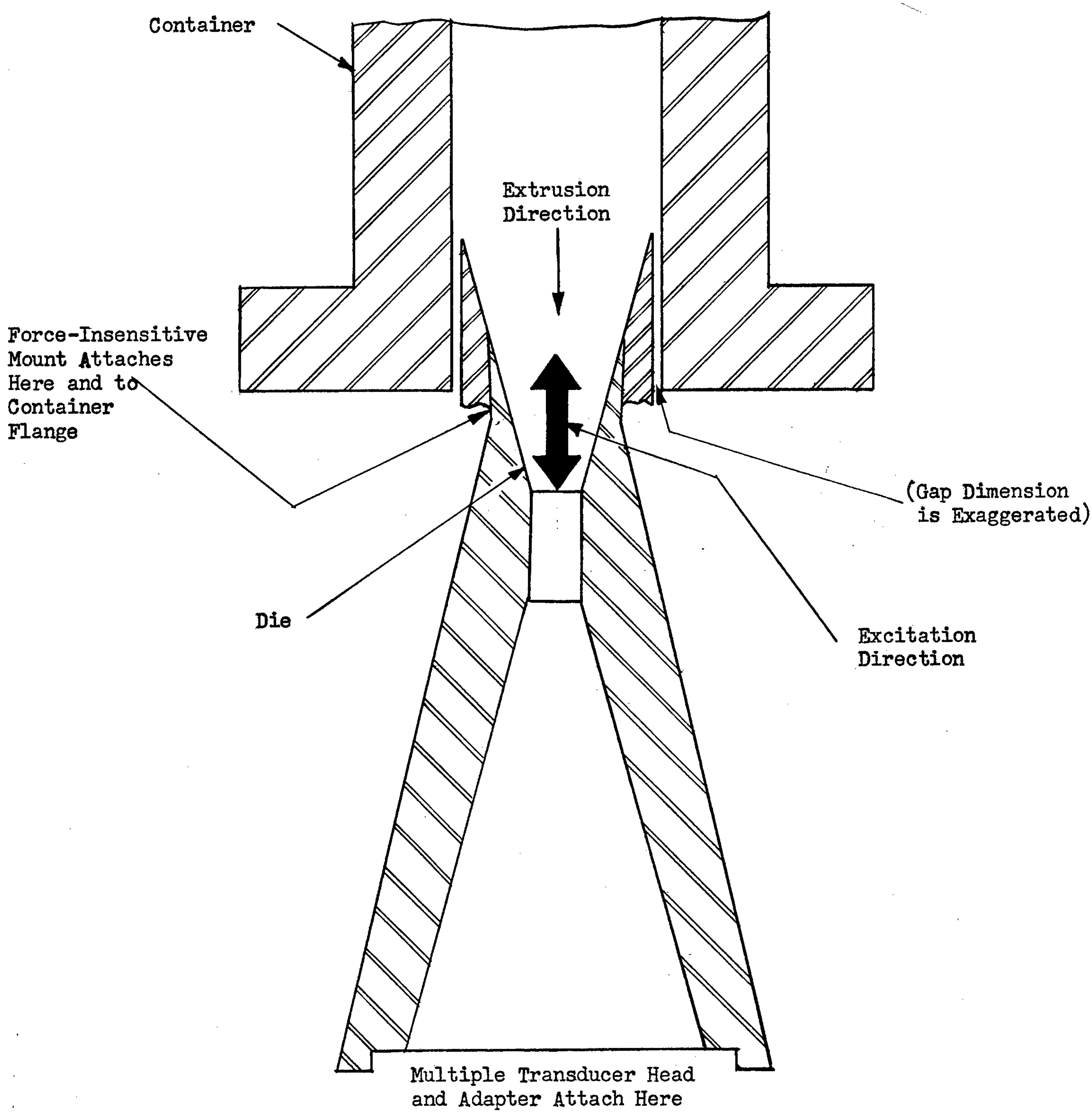

Fig. 1: DIAGRAM OF EXTRUSION DIE AND MOUNTING IN CONTAINER

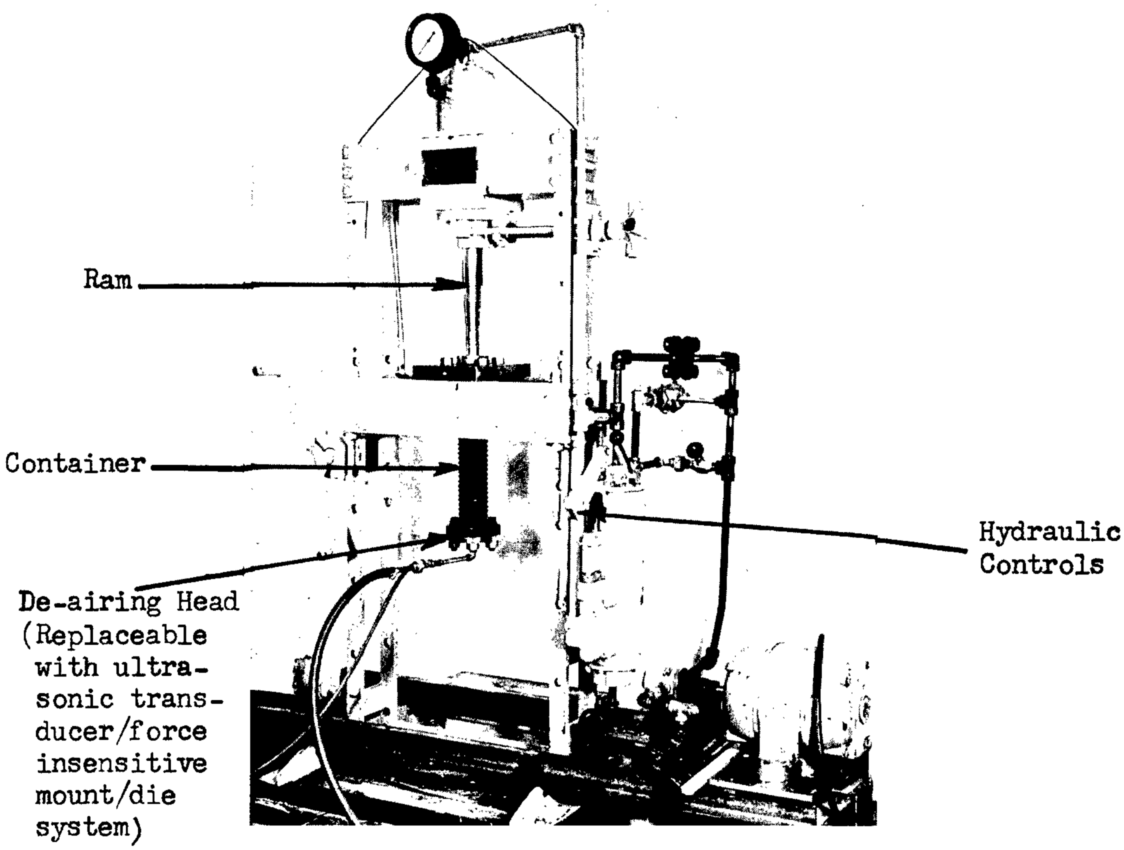

Fig. 2: HYDRAULICALLY OPERATED WILSON PRESS
The de-airing flange is shown on the bottom of the holder.

A 100-ton Wilson hydraulic press of longer stroke was operated in a similar fashion for horizontal extrusion. From this work was evolved an adaptation to a commercially available Loomis press (Fig. 3) of ultrasonic die activation equipment.* This press was provided with a 2-in. diameter container and a tilting mechanism. Successful ultrasonic extrusion was carried out at various head angles.

Dies were prepared for use in the ultrasonic extrusion of 3/8-in. diameter rod (extrusion ratio 13.6 and 26, depending on container diameter), 1/16-in. diameter rod (extrusion ratio 484), and 3/8-in. diameter hexagonal rod (extrusion ratio 26). When the latter was used with a 1/4-in. mandrel, the extrusion ratio was 43. A ribbon die 1/16 in. by 3/4 in. was also used at an extrusion ratio of 50. Conical inlets of 30°, 60°, and 120° included angle, and a bell mouth inlet were variously involved. These dies had land sections of 0.750 in. to 1.5-in. length. The ribbon die was sharp edged with a flat face. All could be successfully activated under the extrusion load.

IV. CERAMIC MATERIALS**

A. Preparation of Materials

Extrusion mixes were prepared in a muller by either dry blending the ceramic and plasticizer and adding the desired amount of water, or by adding a relatively dilute water-plasticizer solution to the ceramic and drying to the desired moisture content. Both methods appeared to yield satisfactory results. The latter method would be expected to provide more uniform mixing but is more time consuming. Certain mixtures obtained from other workers were prepared in their laboratories by essentially the same techniques.

B. Alumina (Fused and Ground)

The bulk of the work made use of Norton 38900 fused alumina as a standard reference material. This material was selected for extrusion because it represents a typical commercial-type alumina with relatively well-known characteristics. This grade of alumina is fused and ground, having solid dense particles, irregular in shape, with a mass median diameter of approximately 7 μ.

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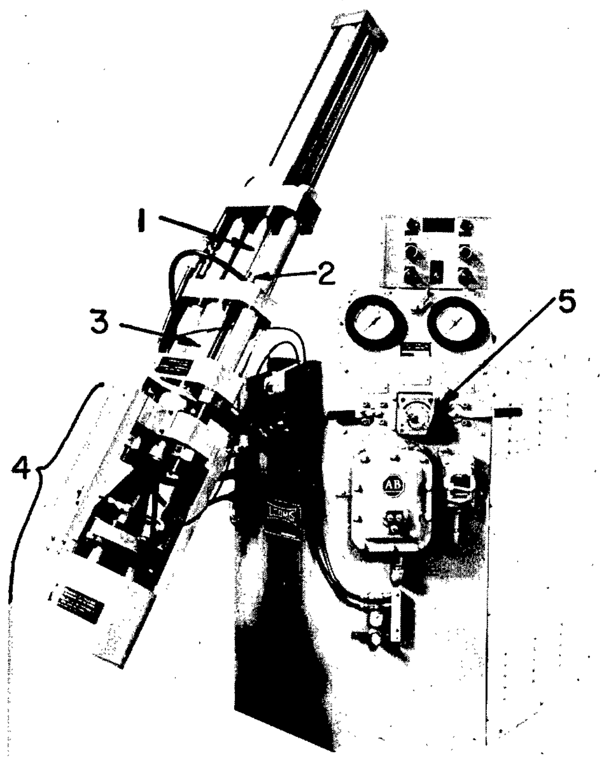
* University of California, LRL.

** Particle size distribution and certain other properties are delineated in the appendix.



1 Ram

2 De-airing Head

3 Container

4 Ultrasonic Transducer/Force Insensitive Mount/Die System Array

5 Hydraulic Controls

Fig. 3: CERAMIC EXTRUSION PRESS WITH ULTRASONICALLY ACTIVATED DIE

C. Alumina (Soft, Polishing)

In addition, Norton E-111-H Alumina was selected because of its radical difference from the other types used, and because it presents somewhat different problems in extrusion. The mass median diameter was found to be in the 3- to 6-μ range; however, the particle shape is irregular and the particles themselves are porous.

D. Mixed Size Alumina

To obtain data for an alumina with good packing characteristics in which any orientation due to ultrasonics would be observable, a blend was made of 70% Norton 38900 and 30% Alcoa T-60 Alumina, having mass median diameters of approximately 7 μ and 115 μ, respectively. Alcoa T-60 Alumina was selected to represent a typical coarse-particle alumina; it is relatively dense, with platelet-shaped particles.

E. Clay

For initial testing, Ajax "P" Clay, supplied by the Georgia Kaolin Company, was used and is representative of flake-like material.

F. Porcelain

This material was supplied premixed with 2 w/o polyvinyl acetate binder and a lower water content than normal for commercial practice.

G. Titania

This was furnished premixed with water and contained 2 w/o of a polymeric binder. Its extrudability was pH-sensitive.

H. Magnesia

Calcined magnesia (International Minerals and Chemical Corporation grade U-99) was also studied as part of the program. This unfused magnesia has a mean particle diameter of 8.25 μ, contains a maximum of 99.5% MgO, and was prepared from magnesium chloride at 2900-3000°F. Calcination at this temperature normally would lead to low rates of hydration. It was observed that this material does hydrate when mixed with cold water. As a result, the moisture content of extrusion formulations decreases with aging and extrusion becomes more difficult. Ammonium alginate was used as a plasticizer in the first experiments, but release of ammonia indicated reaction with hydrated magnesia. Subsequently, sodium alginate was used.

I. Zirconia

A sub-micron, stabilized zirconia, furnished by General Electric Aircraft Nuclear Propulsion, Cincinnati, was extruded in mixtures containing 4 w/o starch, 12 w/o glycerine, and various amounts of water.

V. INVESTIGATION OF ULTRASONIC EXTRUSION PHENOMENA

The first experimental extrusions of 38900 alumina involved qualitative range-finding investigations with a 3/8-in. rod die ultrasonically activated in the axial mode. It was observed that the rate of ram travel increased 47% (from 9-3/4 in./min to 13-1/2 in./min) together with a simultaneous 33% reduction in required force (from 2400 to 1600 lb) compared to the nonultrasonic controls. It was further observed that formulations of reduced water content (from 16% to 13%) could be ultrasonically extruded under nearly comparable conditions (12 in./min ram speed, 1560-lb force). Normal commercial practice utilizes 20-30% water. It was also possible to extrude with ultrasonic die activation under conditions which developed no ram motion without this activation.

A. Effect on Extrusion Pressure and Rate

During much of the experimental work, simultaneous increases in extrusion rate and decreases in pressure occurred with each application of ultrasonics. Typical data for such extrusions are listed in Table 1 and plotted in Fig. 4 and 5. In both cases, the mixtures used could not be nonultrasonically extruded at 2700 psi. From Fig. 4, it appears that power level which is increased above 1000 watts begins to have a decreasing effect; possibly this is because the extrusion rate is nearing the maximum possible for the press. The data for the stiffer composition, shown in Fig. 5, does not level off.

In order to measure these effects separately, investigations were made at constant pressure and also at constant rate. The results at constant pressure are shown in Table 2 and are plotted in Fig. 6. A later series of runs is plotted in Fig. 7, together with a series in which extrusion rate was held constant. The operating limits (especially rate) of the equipment may be responsible for some effects at the ends of the curves. When compared with the more plastic composition, the drier formulation appears to show more change in rate than in pressure for the same increase in ultrasonic power level.

With rate held constant, substantial reduction in pressure requirement occurred with increase in ultrasonic power. With pressure constant, rate increased with ultrasonic power by one or two orders of magnitude for mixes extrudable without ultrasonics, and even more dramatically for mixes extrudable only with ultrasonics.

Table 1

EFFECT OF ULTRASONIC POWER LEVEL ON
EXTRUSION RATE AND PRESSURE

Ultrasonic Frequency: 20 kc/sec

Composition	Ultrasonic Power, watts	Pressure, psi	Extrusion Rate, in./min
A*	0	2700	0
	250	1480	109.5
	550	1210	147.2
	700	800	178.2
	1100	670	190.4
	1300	565	195.8
	1500	590	193.1
B**	0	2700	0
	500	1370	119.1
	1000	1000	152.3
	1350	835	186.7

*	w/o
Alumina 38900	82.5
Ammonium Alginate	1.0
Water	16.5

**	w/o
Alumina 38900	82.8
Ammonium Alginate	0.8
Water	16.4

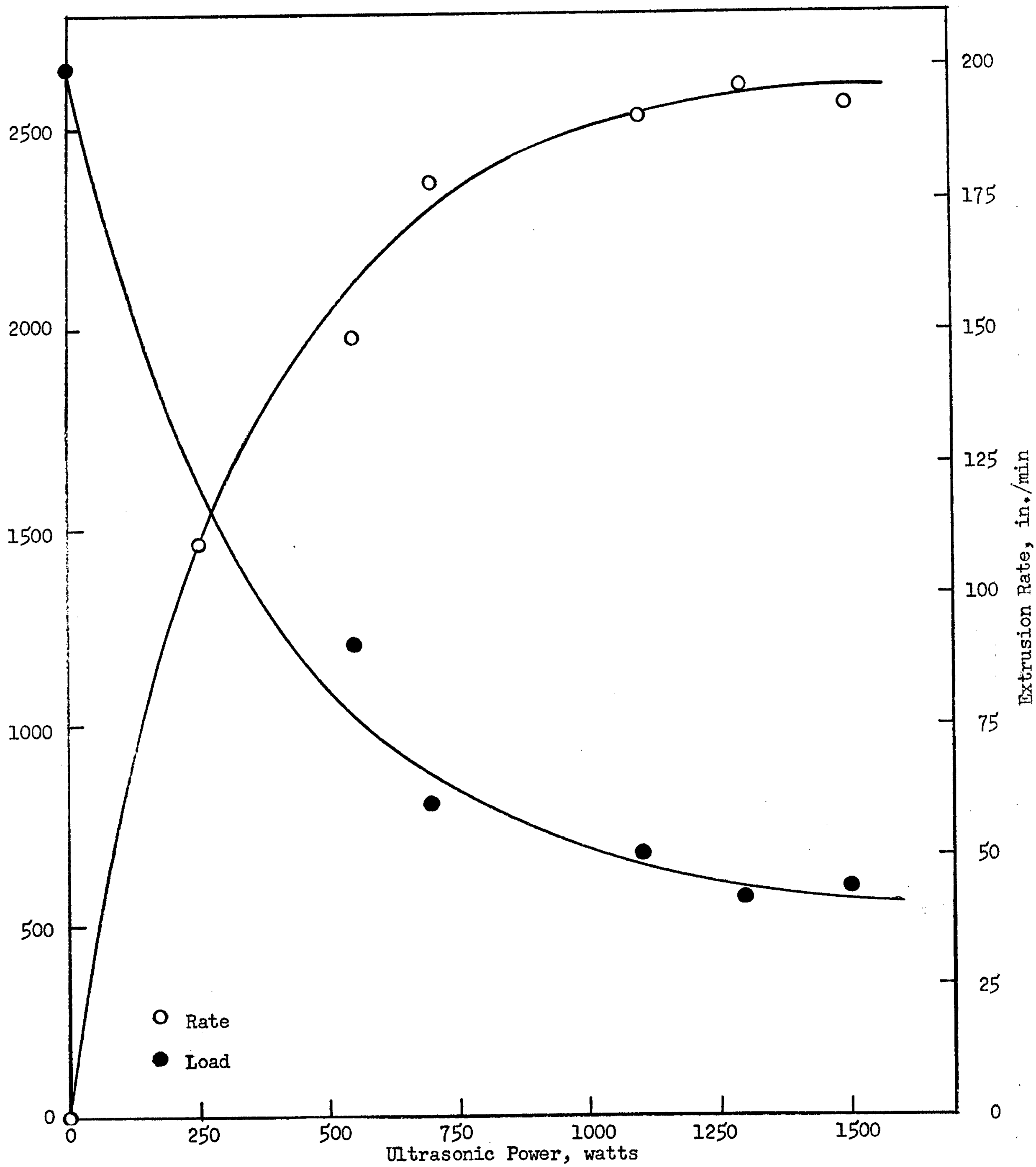


Fig. 4: RELATION OF ULTRASONIC POWER LEVEL TO EXTRUSION RATE AND PRESSURE (From Composition A, Table 1)

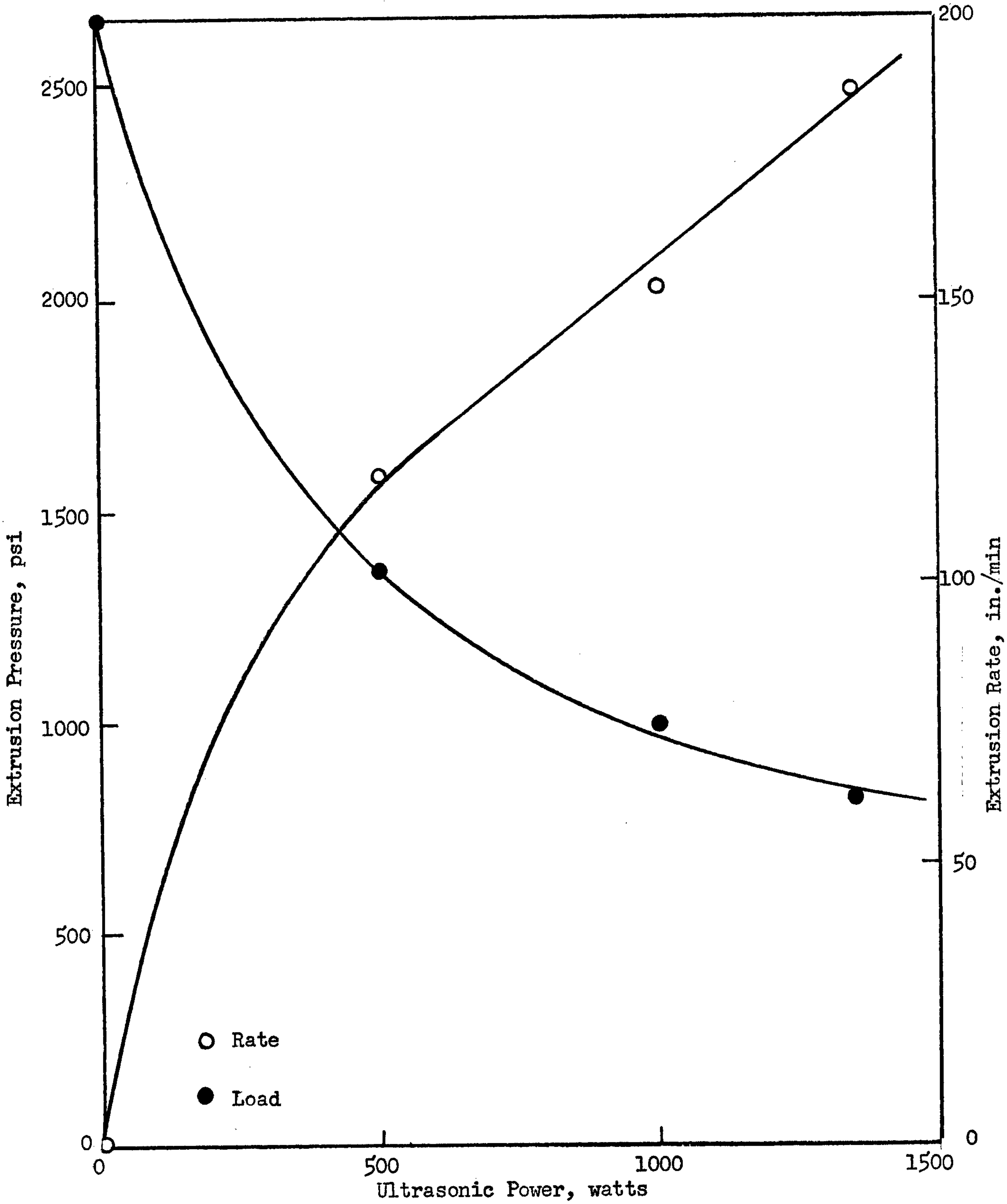


Fig. 5: RELATION OF ULTRASONIC POWER LEVEL TO EXTRUSION RATE AND PRESSURE
(From Composition B, Table 1)

Table 2

EFFECT OF ULTRASONIC POWER LEVEL ON EXTRUSION RATE UNDER CONSTANT PRESSURE*

Die Activation: 20 kc/sec

Extrusion Pressure, psi	Ultrasonic Power, watts	Extrusion Rate, in./min
505	0	0
	800	23
	1200	37
1010	0	0
	400	14
	800	55
	1200	98
2020	0	0
	400	23
	800	138
	1200	178
3370**	0	0
	400	118
	800	242
	1200	***

* Composition:

	w/o
Alumina 38900	84
Water	15
Ammonium Alginate	1
	100

** At 800 and 1200 watts, the pressure did not reach this value during extrusion.

***Too fast to measure.

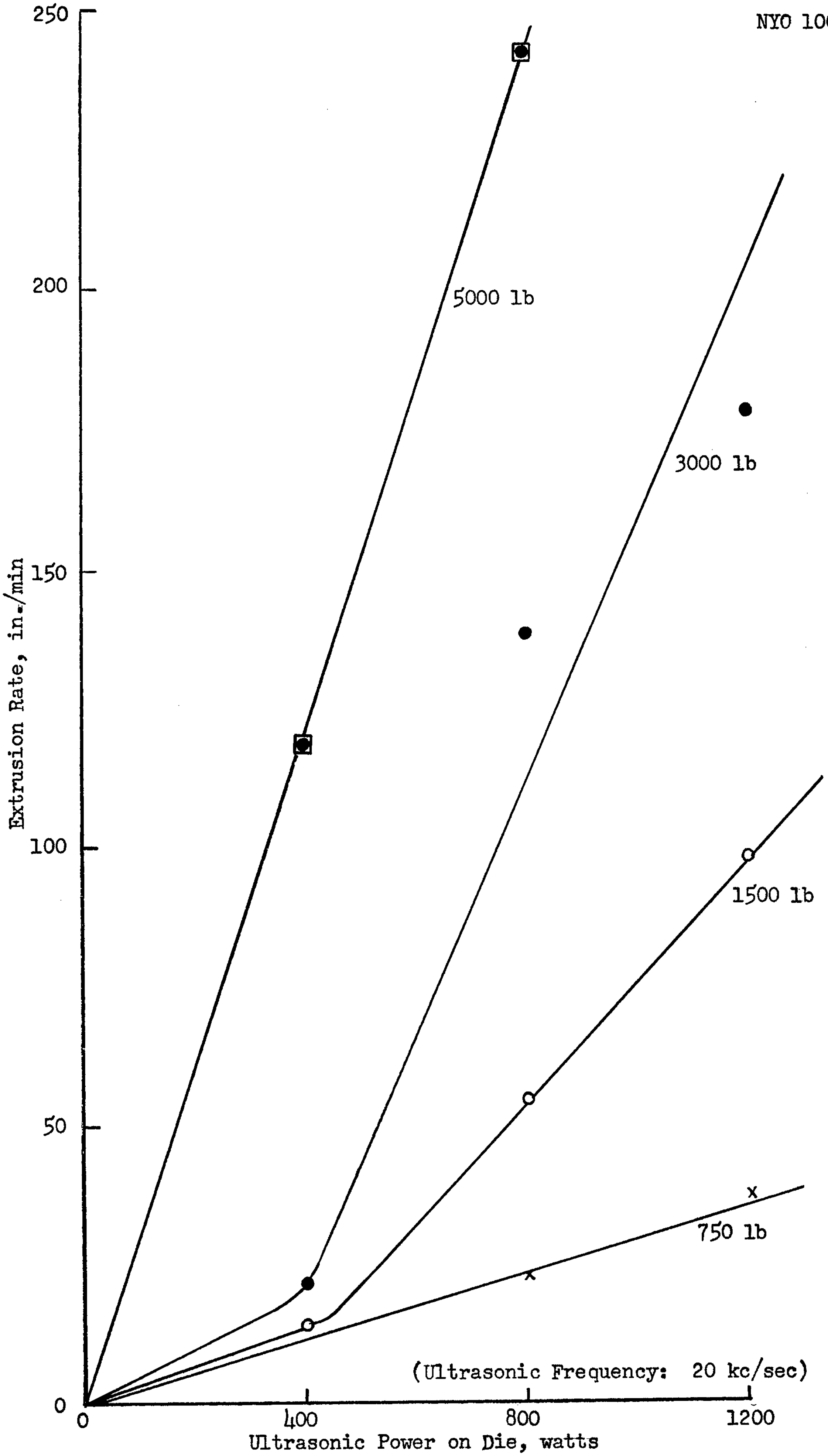


Fig. 6: RELATION OF ULTRASONIC POWER TO EXTRUSION RATE

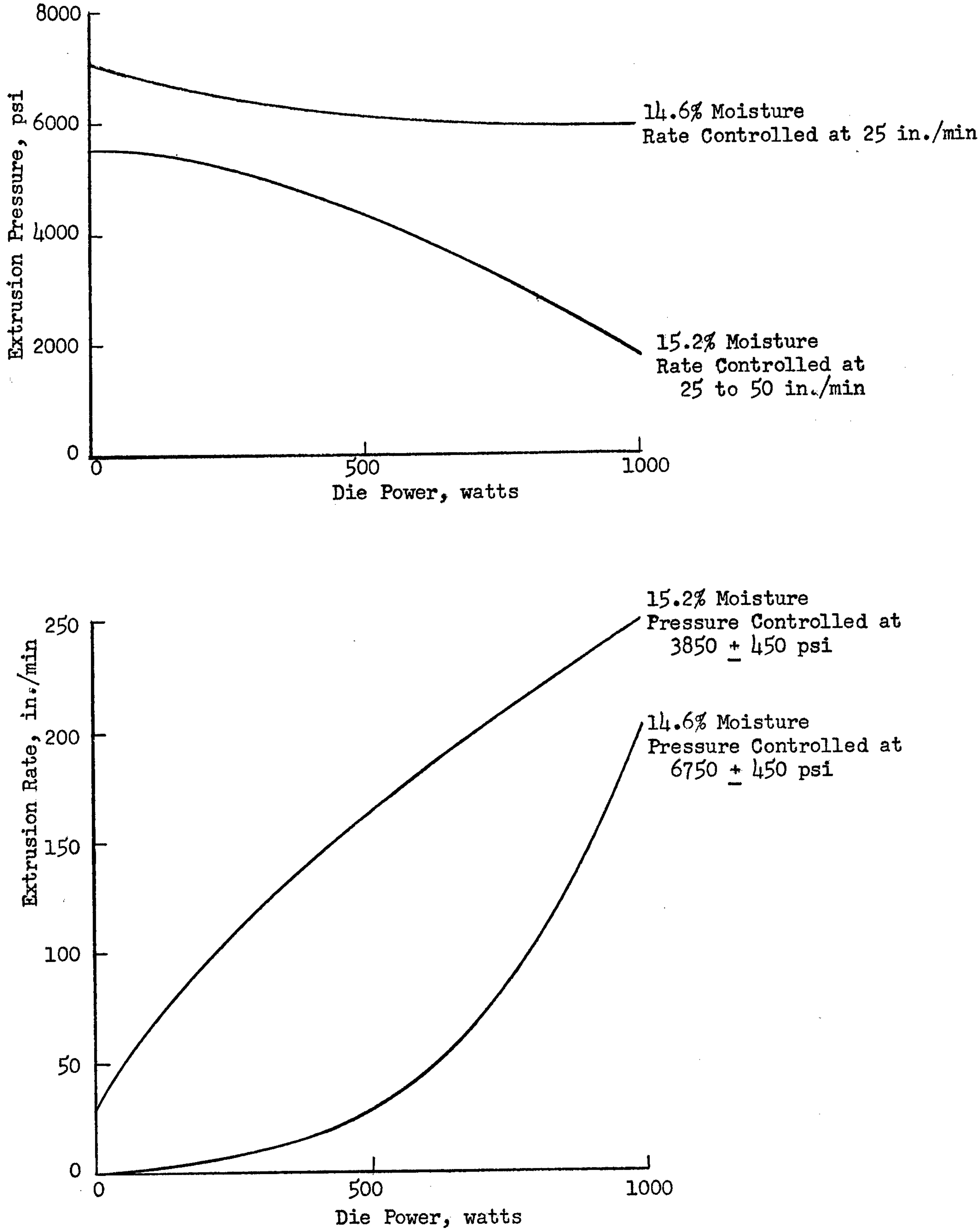


Fig. 7: EXTRUSION PRESSURE AND RATE AS FUNCTIONS OF ULTRASONIC DIE POWER

Norton 38900 Alumina, 2% Ammonium Alginate
Die: 3/8-in. dia; Extrusion Ratio: 13.6

B. Improvement of Surface Finish

During extrusion tests with aged mixes of 38900 alumina containing 17.75 w/o water and 0.25 w/o ammonium alginate, a number of specimens were made which showed marked changes in surface finish. These could be observed in portions of the same rod extruded with and without ultrasonic activation. Typical extrusion data also showed the increased extrusion rate and decreased force required.

	No Ultrasonics	With Ultrasonics*
Maximum extrusion load, psi	10,000	7,000
Extrusion rate, in./min	Nearly 0	121

The typical appearance of the surface, with the roughened, torn, and pock-marked characteristics of Fig. 8A, is not apparent in the corresponding photographs of the ultrasonic extrusion, Fig. 8B. Clearly, the surface characteristics of the extruded shape are improved.

Another surface effect is illustrated in Fig. 9. There is a marked reduction in the amount of metal abraded from the die and picked up on the surface of the extruded specimen. The darkened surface of the specimen becomes increasingly lighter as the power level is increased.

Similar ultrasonic effects in the improvement of surface finish were noted with other materials, notably porcelain and titania (Section VIII), and appear to vary in magnitude with the plasticity of the composition.

C. Effect on Sintered Properties

Several specimens were carried through measurements of green density (after low-temperature drying) and/or fired density and/or modulus of rupture after firing.

The results are listed in Table 3. Apparently, firing conditions exert an overshadowing influence on fired density. Hence, comparisons between series are probably valid only for series C and D, which were fired in the same kiln charge. Preliminary water absorption tests were run on the fired specimens from series A. Within the limits of the test procedure all the ultrasonic specimens absorbed only 75% of the amount of water absorbed by the nonultrasonic control. While the density differences are not large, the highest density after firing in each series was recorded for one of the ultrasonically extruded samples. In the tests for breaking strength, the highest moduli of rupture were found in the samples extruded at the highest ultrasonic power level even though the extrusion pressure was lowest. Comparisons on a statistical series of parallel specimens run at normal and at reduced water content should be made in future work.

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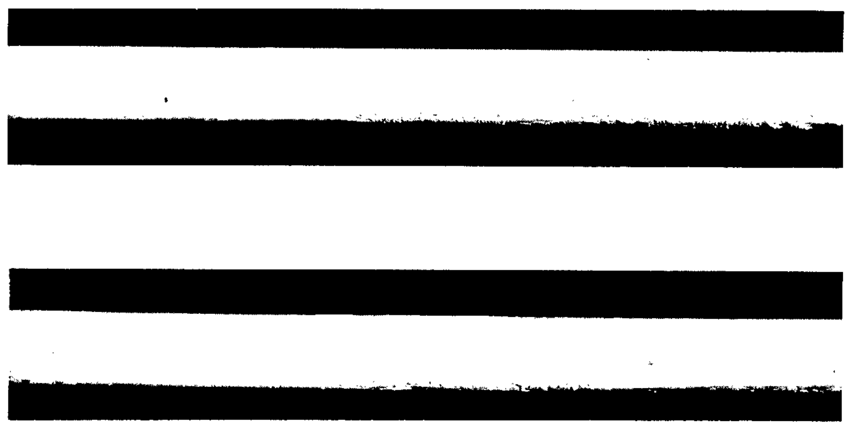
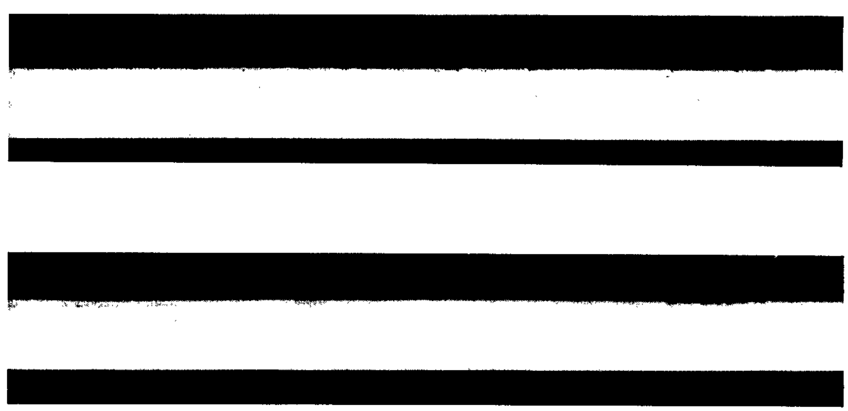
* Axial activation of die at 20 kc/sec, 500 watts.



A. No Ultrasonics



B. With Ultrasonics

Fig. 8: ULTRASONICALLY IMPROVED SURFACE FINISH OF EXTRUSIONS OF ALUMINA 38900 CONTAINING 0.25 PERCENT AMMONIUM ALGINATE

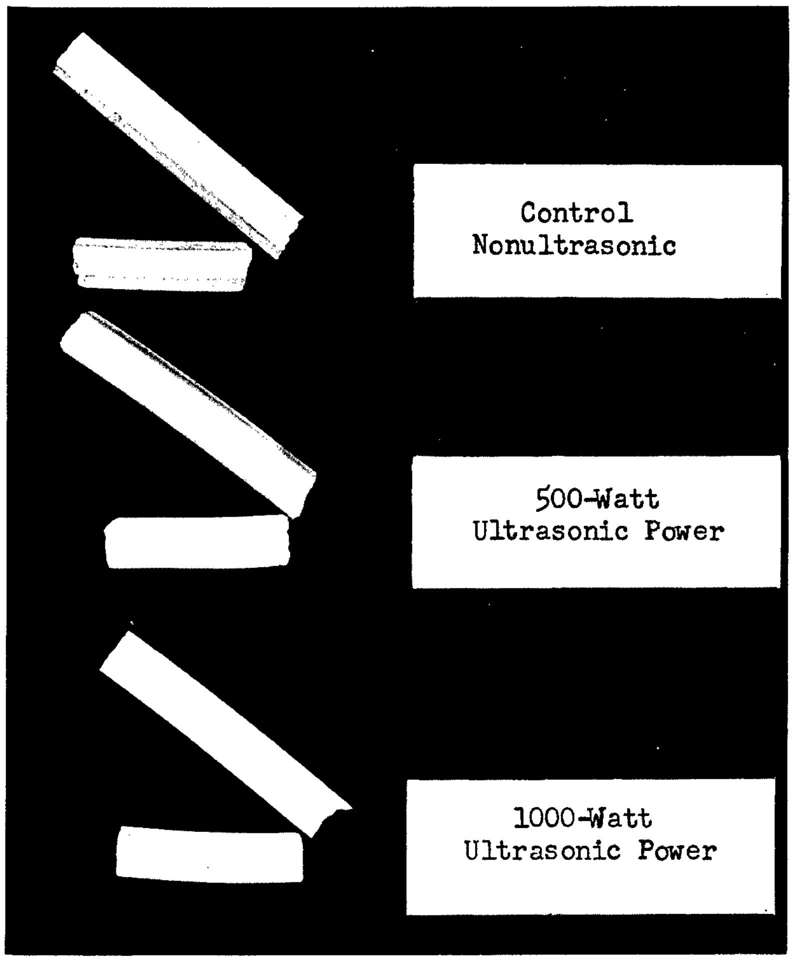


Fig. 9: REDUCTION IN DIE PICK-UP CONCOMITANT WITH ULTRASONIC ACTIVATION OF EXTRUSION DIE (38900 Alumina; Extrusion Ratio: 26)

Table 3

PROPERTIES OF EXTRUDED ALUMINA 38900 AFTER FIRING* AT 3200-3300°F

Diameter of Rod: 3/8 in.
Extrusion Ratio: 13.6
Ultrasonic Frequency: 20 kc/sec

Theoretical Density: 3.95 g/cc
Activation of Die: Axial
Maximum Extrusion Rate: 243 in./min

	Composition of Mix, %			Extrusion			Density, g/cc		Fired Density,	Modulus of Rupture, psi
Series	Alumina 38900	Ammonium Alginate	Water	Pressure, psi	Ultrasonic Power, watts	Extrusion Rate, in./min	Green	Fired	% of Theoretical	$(M) = \frac{8P\ell}{\pi d^3}$
A	82.8	0.8	16.4	5950	0	1	2.33	3.55	89.9	
				3000	500	119.1	2.28	3.50	88.7	
				2200	1000	152.3	2.31	3.55	89.9	
				1850	1350	186.7	2.30	3.58	90.7	
B	83.5	1.0	15.5	5400	0	243		3.41	86.4	
				4600	250	243		3.56	90.2	
				4000	500	243		3.55	89.9	
				3400	1000	243		3.52	89.2	
C	83.8	1.0	15.2	8600	0	52.8		3.32	84.0	19,103
				5200	250	102.0		3.27	82.9	19,807
				2200	1000	150.0		3.40	86.1	20,116
D	82.7	1.0	16.3	3400	0	26.1		3.21	81.3	11,866
				1600	250	103.5		3.34	84.7	15,932
				1000	1000	134.0		3.26	82.6	21,961

* Fired at Ceramics Research Station, Rutgers University.

D. Geometric Considerations in Ultrasonic Activation

1. Site and Mode

The application of ultrasonics axially to the die alone, axially to the die and in the bell mode to the container, and to the container alone, were briefly evaluated. The container was activated by a pair of 20-kc magnetostrictive transducers symmetrically mounted to induce a bell-mode vibration. Identical mixes of alumina were extruded with the results shown in Table 4.

Table 4

EFFECT ON EXTRUSION RATE OF SITE OF APPLICATION OF ULTRASONIC VIBRATION*

Frequency: 20 kc/sec

Application Site	Ultrasonic Power, watts	Extrusion Pressure, psi	Extrusion Rate, in./min
	0	1680	143
Container (Bell)	250	1140	169
Container and Die	250 ea.	940	175
Die (Axial)	250	940	170

*Composition of identical batches of alumina:

	w/o	
Alumina 38900	39.6	
Ammonium Alginate	0.4	
Water	60.0	(Formulation blended, then dried to 16.9 w/o
	100	

In this series, axial die excitation gave the maximum extrusion pressure reduction and extrusion rate increase. Simultaneous vibration of both container and die also resulted in improvement. However, activating the container alone, in the bell mode, resulted in less improvement.

In a later series, extrusions of 38900 alumina formulations were made without ultrasonic excitation, with axial-mode ultrasonic excitation of the die, with flexural-mode excitation of the container, and with combined die and container excitation. At constant rate, the required extrusion pressure was reduced by combination ultrasonic excitation to 810 psi from 4710 psi for nonultrasonic extrusion, as shown in Table 5. Axial excitation of the die alone effected a reduction to 2420 psi.

Table 5

EFFECT OF ULTRASONIC EXCITATION AND SITE APPLICATION ON EXTRUSION OF 38900 ALUMINA

(Formulation contains 15.3 w/o H_2O and 1 w/o plasticizer)

Ultrasonic Frequency: 20 kc/sec
Maximum Extrusion Rate: 240 in./min

Type and Site of Excitation	Ultrasonic Power, watts	Pressure, psi
None (control)	0	4710
Axial excitation of die	1000	2420
Flexural excitation of container	1000	2960
Combined excitation of die and container	1000 ea.	810

Container excitation requires further study to estimate its contribution to the extrusion of low-water content compositions.

2. Container Fill Height

The effect of the quantity of ceramic mix in the container was investigated to determine whether significant differences in extrusion characteristics would result. Batches of 925 g and 350 g were tested under control conditions, and under ultrasonic activation at 20 kc and 1000-watts power level. The quantities of ceramic used resulted in heights of 15.0 in. and 5.5 in. in the 24-in. long container.

The results (Table 6) indicate that a lower height of fill in the container requires a lower extrusion pressure and yields a higher extrusion rate with or without ultrasonics. With either high or low fill, however, ultrasonic energy produced the anticipated important improvements in extrusion pressure requirements and in extrusion rates, and to the equivalent extent. Only modest improvement from cylinder activation alone and the marked improvement from axial die activation, even in 15-in.-long fill, indicate that ultrasonic ceramic extrusion probably involves a mechanism active in the die-approach or die-land zones.

Table 6

EFFECT OF QUANTITY OF FILL ON EXTRUSION

Ultrasonic Frequency: 20 kc/sec
Container: 24 in.
Extrusion Ratio: 13.6

Fill Weight, g	Height in Container, in.	Ultrasonic Power, watts	Extrusion		Ultrasonic Effect	
			Pressure, psi	Rate, in./min	Decrease in Load, %	Increase in Load, %
350	5.5	0	3900	111		
		1000	1210	206	69.0	85
925	15.0	0	4820	79.7		
		1000	1680	190	64.3	138

Composition:

	w/o
Alumina 38900	83.2
Water	16.0
Ammonium Alginate	0.8

E. Intermittent Activation

To determine if the effects of ultrasonic die activation would persist (as was observed in the extrusion of metals (13)) after discontinuing the vibration, two extrusions were made in which the die was activated in pulsed fashion for the extrusion of an equivalent amount of material. The results are listed in Table 7.

In both tests, turning off the ultrasonic energy resulted in immediate increases in extrusion pressure and decreases in extrusion rate. No residual effect of ultrasonics could be observed.

VI. REDUCTION OF REQUIRED PLASTICIZER CONTENT THROUGH ULTRASONIC ACTIVATION

It was observed early in the experimental work that stiffer than normal formulations could be extruded with ultrasonic die activation. This transient increase in plasticity and/or reduction in die friction should lead to improvements in the extruded product. Better dimensional control should result from the greater extruded strength and lower slump of the stiffer mixture. Lower water content should be reflected in less shrinkage on firing and possibly lower porosity in the finished specimen. Preparative procedures are simplified through greater flexibility in water and binder content. Accordingly, the magnitude of possible compositional changes was investigated.

Table 7

EFFECT OF INTERMITTENT DIE ACTIVATION DURING EXTRUSION

Die Activation: 20 kc/sec

Composition	Ultrasonic Activation	Extrusion: Average Rate, in./min	Extrusion: Average Pressure, psi
A	On	201	2700
	Off	101	8080
	On	230	2100
	Off	88	7400
	On	196	2700
	Off	92	7400
	On	184	2100
B	On	203	1610
	Off	122	4040
	On	234	810
	Off	136	3770
	On	243	670

Composition:	A, w/o	B, w/o
Alumina 38900	84.2	83.4
Water	15.0	15.8
Ammonium Alginate	0.8	0.8
	100	100

A. Reduction in Binder Content

A series of mixes of 38900 alumina was prepared with water content (between 16 and 18 w/o) and ammonium alginate (between 0.1 and 2.0 w/o) as variables. Each was extruded with and without axial ultrasonic activation of the die at 500-watts input to the transducers, and the extrusion pressure and rate were observed. Comparison of these data is given in Table 8, and a curve showing the effect on pressure is shown in Fig. 10.

Below a concentration of 2 w/o ammonium alginate, the extrusion rates decreased, and the pressure requirement increased markedly for the nonultrasonic extrusions; at 0.2 w/o, the extrusion rate dropped to 28.6 in./min with the pressure increased to 4040 psi. The ultrasonic run at 0.2 w/o extruded at 173 in./min with a pressure of only 1350 psi, comparing roughly with the nonultrasonic run at 1.5 w/o. At 0.1 w/o, the mixture could not be extruded satisfactorily, either with or without ultrasonics, at 20,200 psi.

It appears that with ultrasonic activation, comparable extrusion performance of a non-clay ceramic mix can be obtained with from one-eighth to one-tenth the quantity of binder. All experiments which followed this series included at least 1 w/o ammonium alginate (50% of the amount required for good extrusion without ultrasonics), which gave adequate binding in the as-extruded and green shapes.

B. Reduction of Liquid Content

An observation common to all of the experimental extrusions was that the reduced-pressure, increased-rate effect of ultrasonics is even greater when the plasticity of the ceramic mix is marginal. Mixes too dry and stiff to be extruded without ultrasonics were found readily extrudable with ultrasonic activation. Figure 11 shows the physical appearance of such a mix compared with one of normal stiffness. Table 9 is a compilation of pertinent data from tables appearing elsewhere in this report.

Range-finding tests were conducted on an alumina 38900 mix that was air-dried to obtain lots with different water concentrations. Three samples were extruded with a power input of 500 watts. The results, in Table 10, show that without ultrasonics, a pressure of 4040 psi was required to extrude the ceramic material at 18 w/o, but, under the same conditions with ultrasonic treatment, the sample required only 940 psi. At lower concentrations of water (16.6 and 16.3 w/o) the ceramic mixture could be extruded only with an ultrasonically activated system.

An additional experiment was then performed in which progressively lower water contents were used. The test extrusions were performed at the 1200-watt ultrasonic power level. The results are listed in Table 11 and shown graphically in Fig. 12 and 13. Figure 12 shows the effect on extrusion

Table 8

EXTRUSION OF 38900 ALUMINA WITH AMMONIUM ALGINATE (SUPERLOID)

Water Content: 16-18 w/o
Die Diameter: 3/8 in.
Extrusion Ratio: 13.6

Ammonium Alginate, w/o	Water, w/o	Condition*	Maximum Extrusion Pressure, psi	Extrusion Rate, in./min
0.1	18.0	Control	20,200	**
		Ultrasonic	20,200	**
0.2	18.0	Control	4,040	28.6
		Ultrasonic	1,350	173
1.0	16.0	Control	2,020	136
		Ultrasonic	940	181
1.5	17.1	Control	1,610	163
		Ultrasonic	810	204
2.0	17.9	Control	810	204
		Ultrasonic	610	204

* Control - no ultrasonic activation; ultrasonic-die ultrasonically activated in axial mode at a frequency of 19.8 kc and 500-watts input.

** Extrusion stopped as maximum press load was reached.

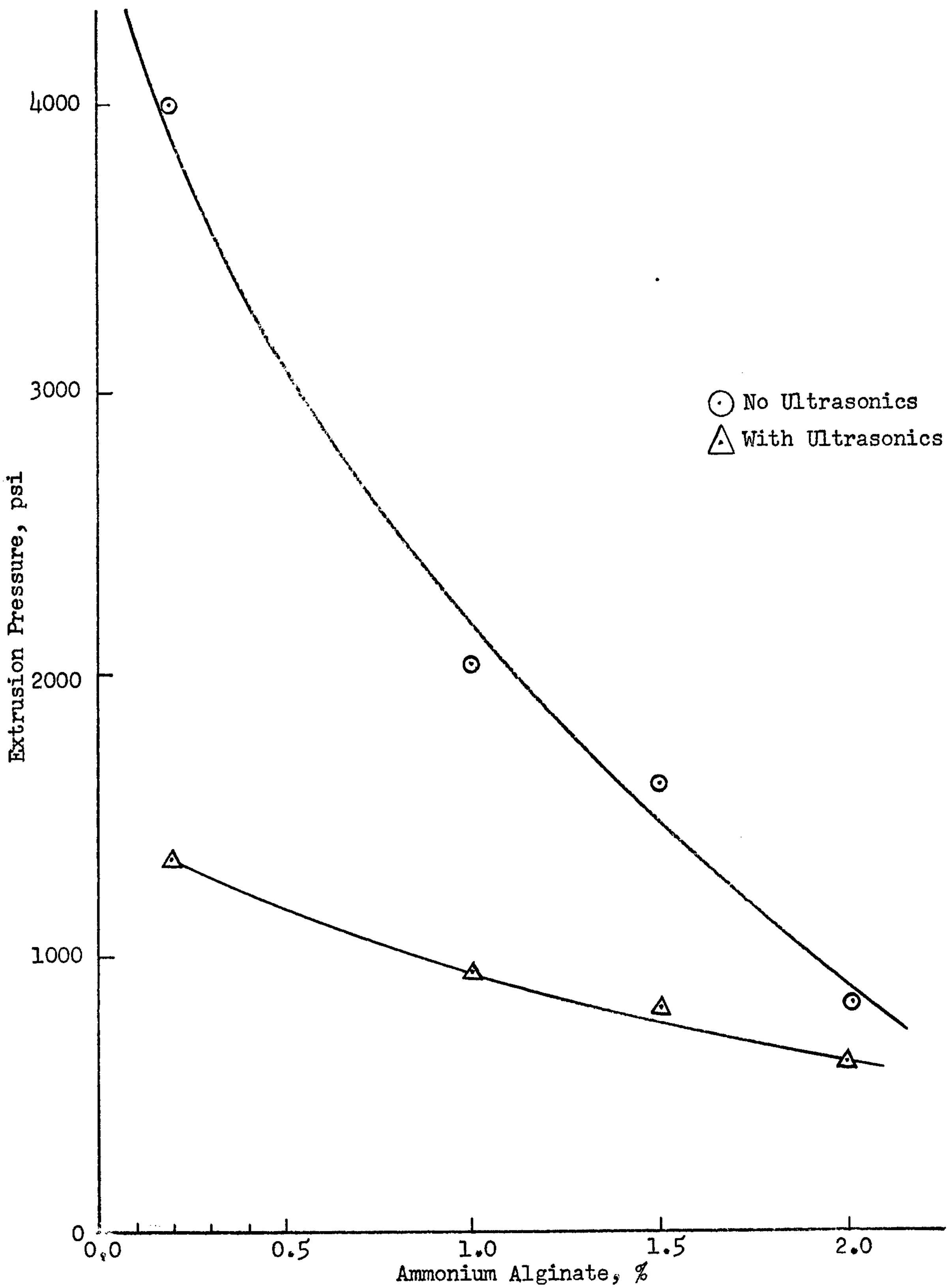


Fig. 10: EFFECT OF ULTRASONIC EXTRUSION ON REQUIRED AMMONIUM ALGINATE CONCENTRATION IN 38900 ALUMINA COMPOSITIONS

Fig. 11: DRY MIX (RIGHT) THAT CAN BE EXTRUDED ONLY WITH ULTRASONICS COMPARED WITH MIX OF NORMAL CONSISTENCY (LEFT)

Table 9

SUMMARY OF DATA SHOWING ULTRASONIC EXTRUSION OF
ALUMINA 38900 MIXES TOO DRY TO EXTRUDE WITHOUT ULTRASONICS
Extrusion Ratio: 13.6

Moisture Content, w/o	Container Pressure, psi	Ultrasonic Power, watts	Extrusion Rate, in./min	Reference, Table
16.5	2700	0	0	1
	1210	550	147	
	565	1300	196	
16.4	2700	0	0	1
	1370	500	119	
	840	1350	187	
15.0	3370	0	0	2
	2020	800	138	
	2020	1200	178	
13.4	6730	0	0	12
	6730	1200	23	
12.6*	4040	0	0	12
	4040	1300	100	

* Different lot of 38900 alumina. See Table 12 and Appendix for details.

Table 10

EFFECT OF VARYING WATER CONCENTRATION
IN ALUMINA ON EXTRUSION PRESSURE

Preset Maximum Pressure: 4040 psi
Ultrasonic Power Input: 500 watts

Test No.	Composition, w/o		Extrusion Pressure, psi	
	Alumina*	Water	Control	Ultrasonic
1	81.0	18.0	2020	940
2	82.4	16.6	No extrusion	2700
3	82.7	16.3	No extrusion	4040

* 1.0% Ammonium Alginate

Table 11

EFFECT OF VARYING WATER CONCENTRATION
IN ALUMINA* ON EXTRUSION RATE

Extrusion Ratio: 13.6
Die: 3/8-in. round

Water Content w/o	Extrusion Pressure, psi		Extrusion Rate, in./min	
	Without Ultrasonics	With Ultrasonics	Without Ultrasonics	With Ultrasonics
18.3	1610	--	201	--
17.8	1750	--	201	--
16.9	3630	--	82.6	--
16.7	--	670	--	228
16.5	4040	--	82.9	--
	--	940	--	225
16.1	--	1210	--	221
16.0	6730	--	13.8	--
15.4	--	2960	--	158
15.1	--	4310	--	118
14.5	--	5120	--	86.8

* Alumina 38900; 1 w/o ammonium alginate; water as shown.

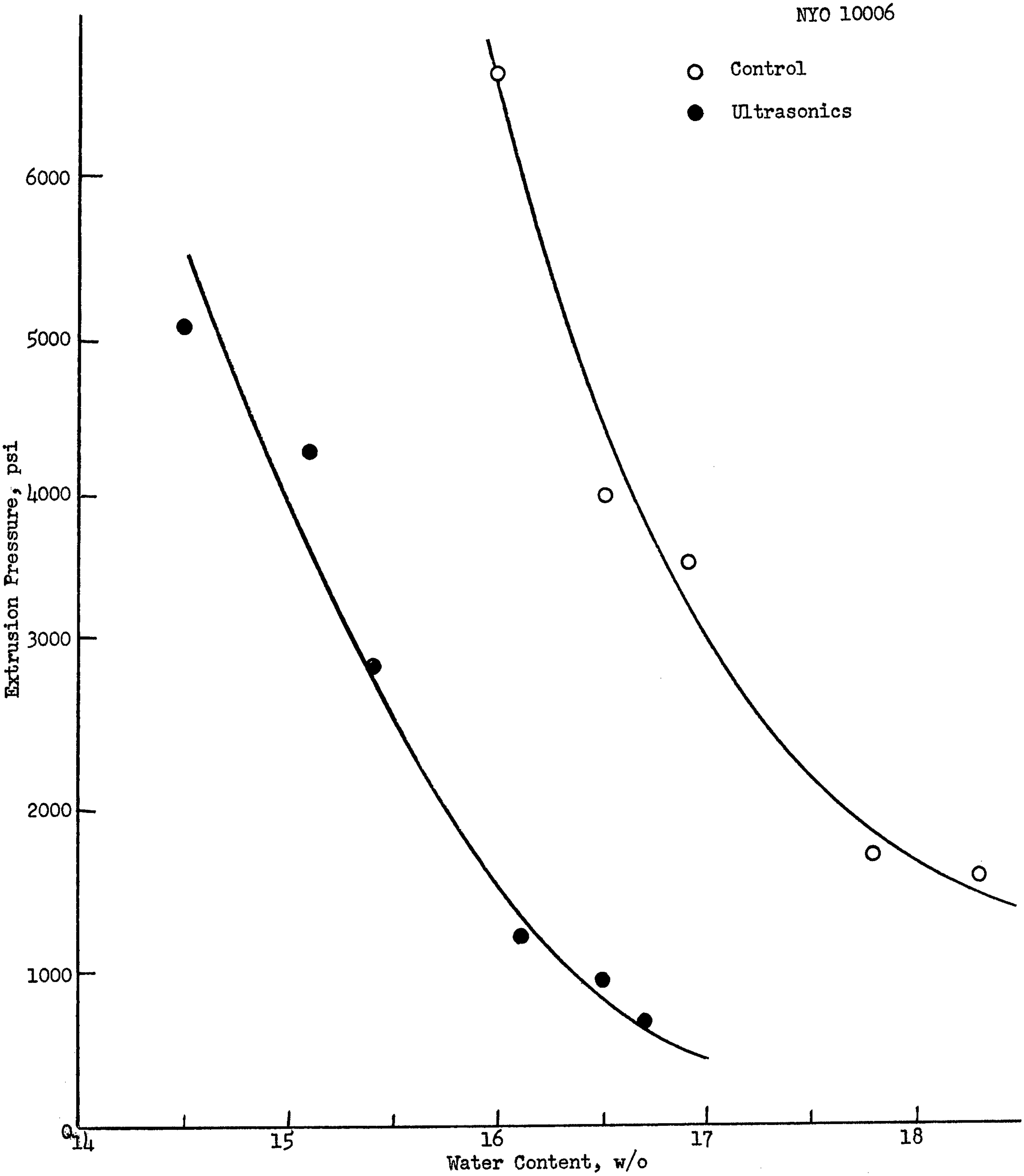


Fig. 12: RELATIONSHIP OF WATER CONTENT TO EXTRUSION PRESSURE IN EXTRUDING ALUMINA WITH AND WITHOUT ULTRASONICS

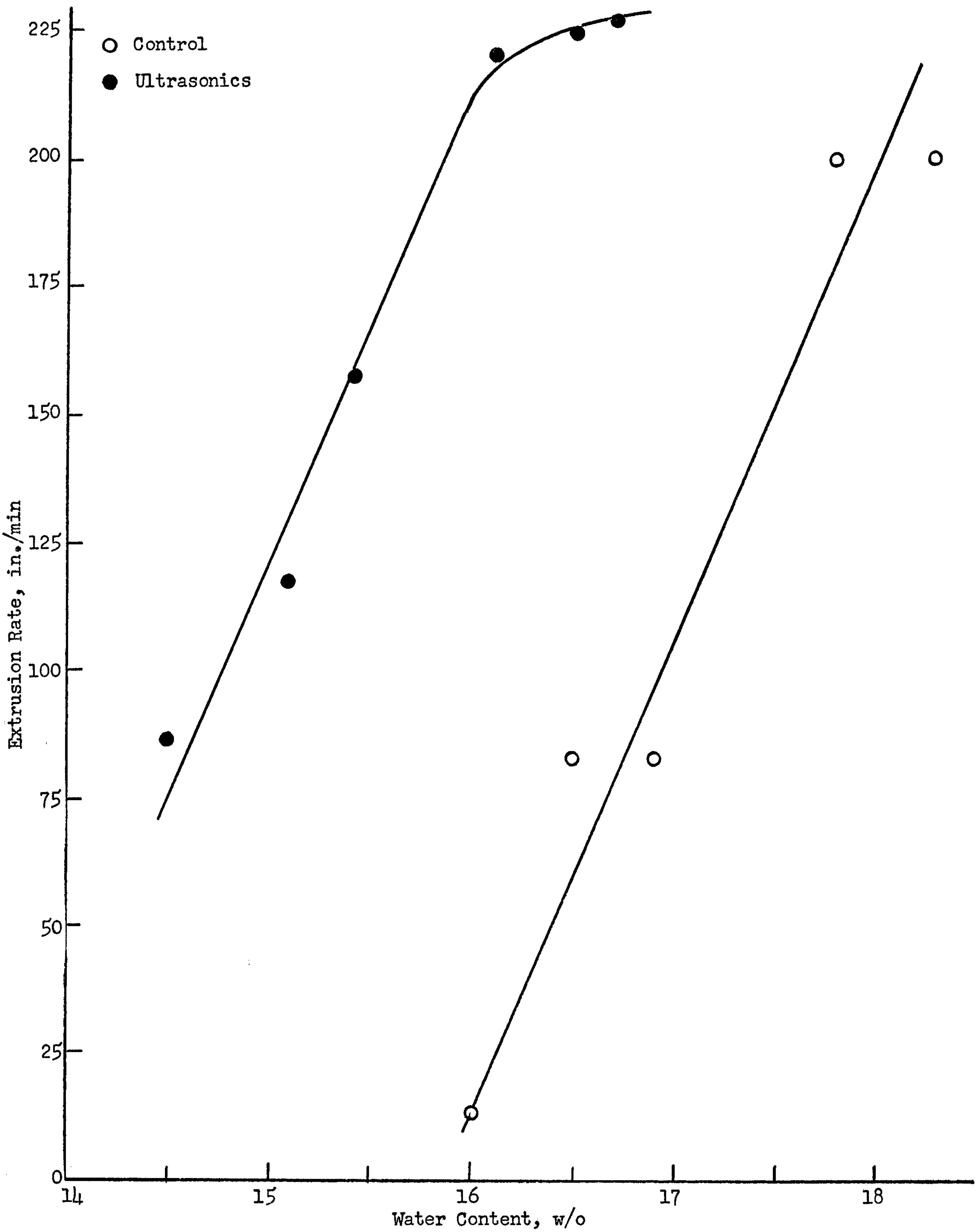


Fig. 13: RELATIONSHIP OF WATER CONTENT TO EXTRUSION RATE IN EXTRUDING ALUMINA WITH AND WITHOUT ULTRASONICS

rate. The control series could not be extruded with less than 16 w/o water; at that concentration, a pressure of 6,730 psi was required. The ultrasonically treated series was extruded at the lowest water concentration, 14.5 w/o, with a pressure of 5,120 psi. At 18 w/o water, the pressure requirement with ultrasonics is only 12% of that required without ultrasonics. For a given extrusion pressure, the water content can also be materially reduced when ultrasonic power is applied.

These tests were extended in later experiments to mixes containing only 13.4 w/o water, and to mixes of a new lot of alumina 38900 (smaller particle size; MMD - 4.7 μ) containing 12.6 w/o water. Results are tabulated in Table 12. In both experiments, extrusion failed to take place without ultrasonics at water contents below 15 w/o. With the first lot of 38900 alumina, extrusion proceeded satisfactorily at 13.4 w/o water and 1200-watts ultrasonic input, representing a water content 14% below the minimum extrudable without ultrasonics. With the second lot, at 12.6 w/o water and 1300-watts power level, a 100-in./min extrusion rate was achieved. The water content in this case was only 85% of the minimum contained in extrudable control mixes, or 40-60% of that used in commercial practice.

Table 12

ULTRASONIC EXTRUSION OF ALUMINA 38900
WITH VARYING WATER CONTENT

Ammonium Alginate: 1 w/o
Ultrasonic Frequency: 20 kc/sec
Extrusion Ratio: 13.6

H_2O, w/o	Extrusion Pressure, psi	Ultrasonic Input, watts	Extrusion Rate, in./min
15.5	10,000	0	45
14.2	10,000	0	0
		1000	53
13.4	10,000	0	0
		400	5
		800	16
		1200	23
15.2*	6,000	0	26
12.6*	6,000	0	0
		1300	100

* These runs were made with a different lot of 38900 alumina having a smaller mean particle size (4.7 μ) and an ammonium alginate content of 2 w/o.

VII. EXTRUSION OF NONCYLINDRICAL AND HOLLOW SHAPES

As mentioned in Section III, a brief investigation of ultrasonic extrusion die geometry was carried out.

A. Hexagonal Rods and Tubes

A series of extrusions of 38900 alumina was conducted using a 3/8-in. hexagonal die, with and without a 1/4-in. round mandrel. The extrusion ratios were 26 and 43, respectively. The expected reduced-pressure, increased-rate effect of ultrasonics was observed to be about the same as previously noted at 14.5 w/o water content. Extruded shapes are illustrated in Fig. 14, and data is presented in Fig. 15. The flat external surfaces of these shapes show tears and cracks and excess of pickup in the control compared with the smooth, virtually uncolored, surface of the ultrasonic specimens.

B. Ribbons

A 100-ton press was equipped with an ultrasonically activated extrusion die of 1/16- by 3/4-in. cross section for extrusion of ribbon-like shapes. This array had an extrusion ratio of 50. A test extrusion was made using soft plastic alumina 38900 mix of 2 w/o binder and more than 18 w/o water content; the pressure requirements versus ultrasonic power are plotted in Fig. 16. Although a satisfactory extrusion resulted, the run-out requirements were not met for such a non-self-supporting shape. The expected reduction in ultrasonic extrusion pressure was observed.

C. High Extrusion Ratio Rods

Also extruded, at a ratio of about 500 to 1, were 1/16-in. diameter rods of alumina E-111-H. The alumina E-111-H contained 1 w/o ammonium alginate and 22.4 w/o water. The pressure on the extrusion container was 6,730 psi. No extrusion took place without ultrasonics. With 1000-watts ultrasonic input to the die, extrusion occurred at 24-in./min, giving rods that retained their structure through drying and firing. Titania, Fig. 17, was also extruded in this geometry (see Section VIII for data).

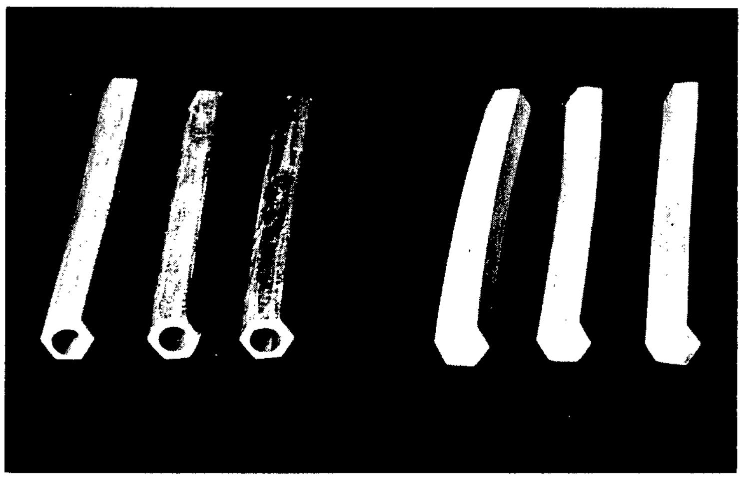


Fig. 14: SOLID AND HOLLOW HEXAGONALLY EXTRUDED ALUMINA 38900

In each type, the nonultrasonic control is at the right and shows more pickup of color from the die than the ultrasonic pieces.

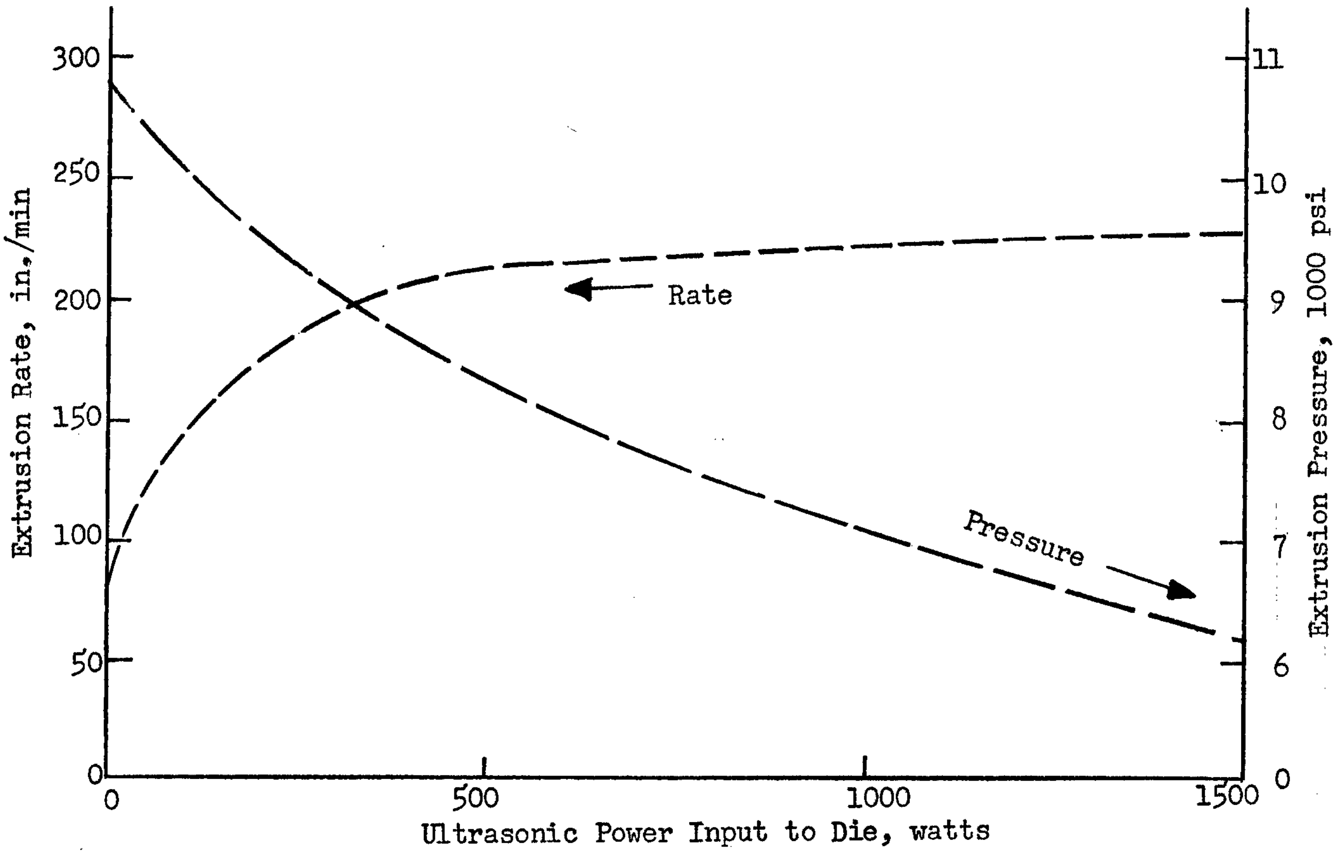


Fig. 15: EXTRUSION OF HOLLOW CERAMIC HEXAGONAL TUBING

Norton 38900 Alumina
H_2O: 14.5 w/o
Ammonium Alginate: 2 w/o

Pressure, psi	Rate, in./min	Power, watts
10,800	68	0
8,400	215	500
7,000	222	1000
6,200	230	1500

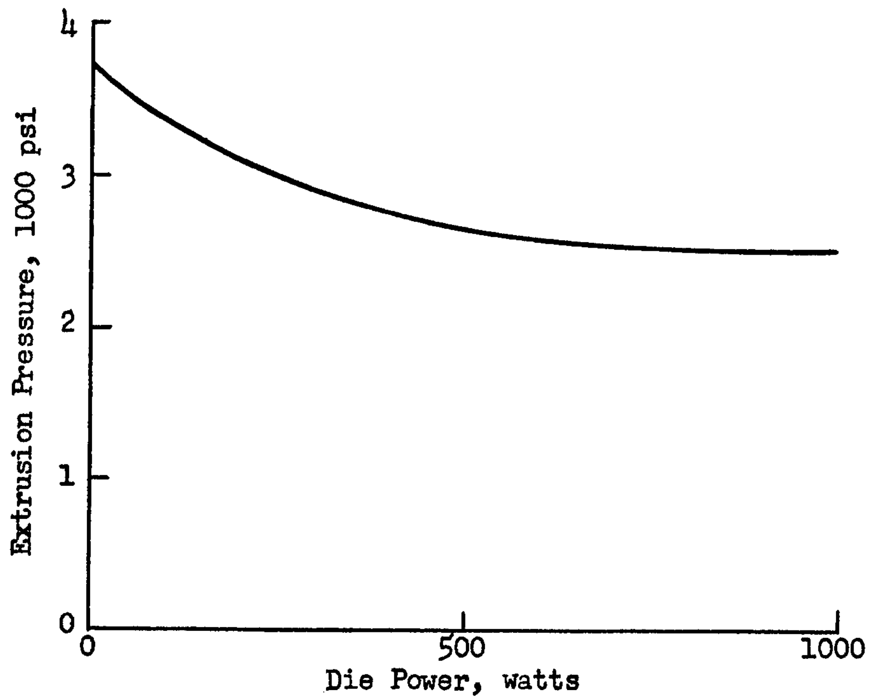


Fig. 16: EXTRUSION PRESSURE AT CONSTANT RATE AS A FUNCTION OF DIE POWER

Norton 38900 Alumina; Ammonium Alginate: 2 w/o

Ribbon: 1/16 in. x 3/4 in.; Extrusion Ratio: 50

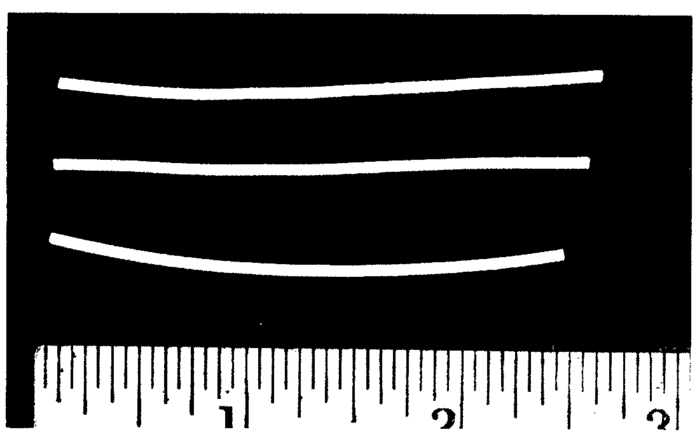


Fig. 17: SAMPLES OF 1/16-INCH TITANIA RODS EXTRUDED WITH ULTRASONIC ACTIVATION (TOP AND MIDDLE) AND WITHOUT ULTRASONIC ACTIVATION (BOTTOM)

VIII. ULTRASONIC EXTRUSION OF A RANGE OF CERAMIC MATERIALS

In order to demonstrate the broad applicability of ultrasonic extrusion, several non-clay ceramics of interest for nuclear applications, or simulants of these, were briefly examined. Data on certain other materials, such as porcelain and titania, studied under related projects are included here for comparison.

A variety of plasticizers was involved in these extrusions. In all cases, ultrasonic effects were noted.

A. Mixed Particle Size Alumina

A mixture of alumina 38900 with larger particle-flake alumina was studied. The latter was obtained from Alcoa T-60 by screening (through 115 mesh, on 150 mesh) to obtain a median particle size of approximately 100 μ. The 100-μ fraction was blended with 7-μ alumina 38900 in the ratio 30:70. The extrusion data (Table 13) indicated generally the same ultrasonic effect as that obtained with alumina 38900 alone. The required extrusion load, at constant rate, was cut almost in half at 500-watts ultrasonic power level, and to about one-third at 1000 watts.

Photomicrographs (Fig. 18) of the fracture surface indicate that no separation or preferential migration of the larger sized particles occurred during ultrasonic activation.

Table 13

ULTRASONIC EXTRUSION OF ALUMINA OF MIXED PARTICLE SIZES

Composition: Alumina 38900 (7 μ): 70 w/o
Alumina T-60 (100 μ): 30 w/o
Ultrasonic Frequency: 20 kc/sec
Active Die: 3/8-in. OD
Extrusion Ratio: 13.6

Mix Composition			Ultrasonic Power Input, watts	Pressure, psi	Extrusion Rate, in./min
Alumina, w/o	Water, w/o	Ammonium Alginate, w/o			
86.4	10.9	2.7	0	4800	40.5
			500	2700	40.5
			1000	1600	40.0
84.0	13.4	2.6	0	2400	40.5
			500	1500	40.5
			1000	670	43.0

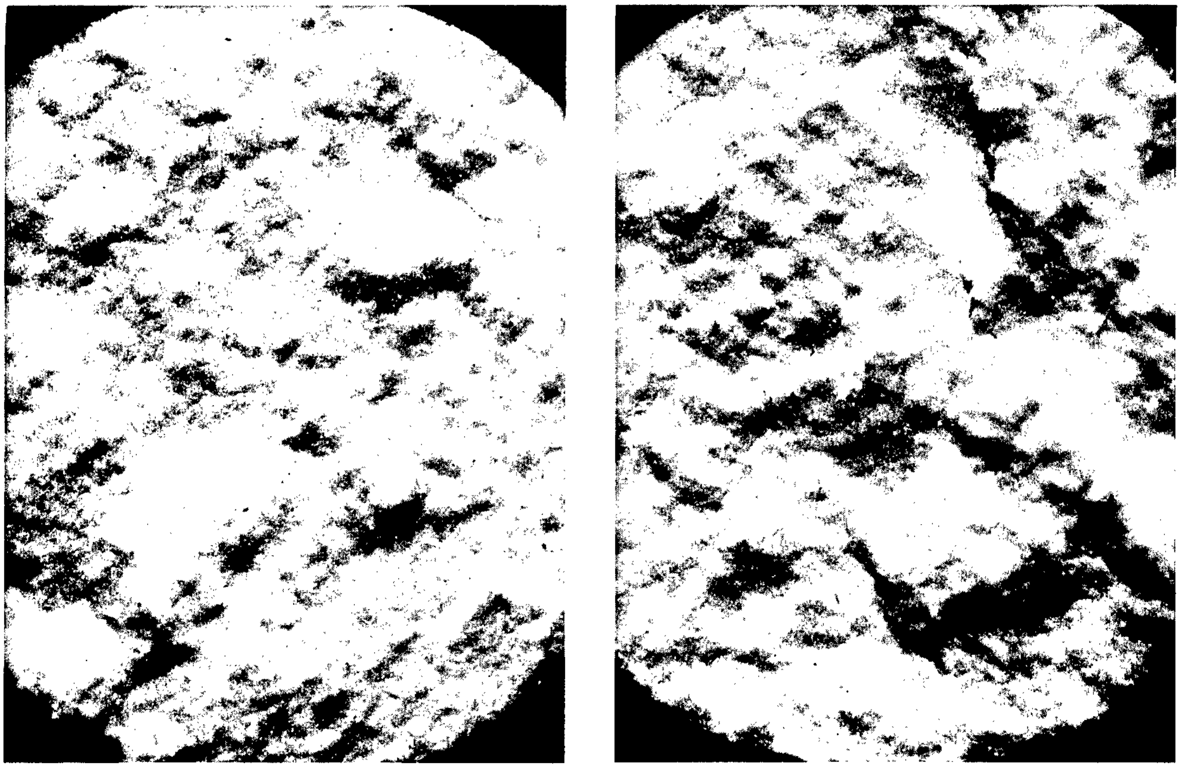


Fig. 18: PHOTOMICROGRAPHS OF FRACTURE SURFACE OF EXTRUDED AND FIRED SPECIMENS MADE FROM MIXED PARTICLE SIZE ALUMINA

Left specimen, nonultrasonic control; right specimen, ultrasonic extrusion. Note similar distribution of larger flake-like particles.

Magnification: 11X

B. Norton E-111-H Alumina

This porous grade of alumina was extruded under various conditions. Table 14 lists data showing the effect of different modes of ultrasonic activation, and of water content. Container excitation was ineffective, while die activation reduced the extrusion pressure to 54% of the control value. Table 15 lists typical data showing the effect of ultrasonics on extrusion rate and pressure at various moisture levels. The effect on pressure requirements was about the same at each level of moisture content. Extrusion rates were increased by ultrasonics. The range of moisture content yielding extrudable compositions was very narrow, possibly limited on the lower end by the pore volume. Nevertheless, considerably stiffer mixtures resulting from reduction in water content, were extrudable with ultrasonics.

C. Ajax P Clay

In order to provide a comparison with the more common types of ceramic extrusion, an extrusion experiment with a clay specimen was carried out. Ajax P clay, a standard ceramic material, was mixed with water containing 1.0% ammonium alginate in the Lancaster muller, following the same technique used for the alumina mixes. The final composition was as follows:

	w/o
Ajax P Clay	80.0
Ammonium Alginate	0.2
Water	19.8

Under conditions that gave reasonably satisfactory extrusion without ultrasonics, the effect of ultrasonic die activation (frequency: 19.8 kc/sec; power: 500-watts input) was observed as follows:

	Control	With Ultrasonics
Maximum Pressure During Extrusion, psi	4500	3900
Extrusion Rate, in./min	67.5	88.4

It should be noted that extrusion can be accomplished at a 31% increase in speed with a simultaneous reduction of 13% in extrusion pressure, when ultrasonic vibration is applied to a typical mix.

Table 14

EFFECT OF ULTRASONIC EXCITATION AND SITE OF APPLICATION ON EXTRUSION OF E-111-H ALUMINA

Ultrasonic Frequency: 20 kc/sec
Die Diameter: 3/8 in.
Extrusion Ratio: 13.6
Formulation contains 1 w/o plasticizer

H_2O, w/o	Type and Point of Excitation	Ultrasonic Power, watts	Pressure, psi	Rate, in./min
22.1	None (control)	0	6,730	Did not extrude
	Flexural excitation of container	1000	6,730	11.3
22.5	None (control)	0	6,730	103
	Axial excitation of die	250	5,000	240*
		500	4,450	240*
		1000	3,640	240*

* Maximum extrusion rate.

Table 15

EXTRUSION OF NORTON E-111-H ALUMINA

Rod Diameter: 3/8 in.
Extrusion Ratio: 28

Dry Formulation:	w/o
Ammonium Alginate	2
Norton E-111-H Alumina	98

Moisture Content, w/o	Ultrasonic Power to Die, watts	Pressure, psi	Rate, in./min
20.2	0	6000	151
	500	4200	151
	1000	2600	151
22.0	0	5200	119
	500	4000	117
	1000	2200	117
22.4	0	4000	75
	500	2000	126
	1000	1500	197

D. Magnesia

Unfused magnesia reacts with water to form magnesium hydroxide; the latter, when wet, is sufficiently alkaline to liberate ammonia from ammonium salts, and to react with atmospheric carbon dioxide to form magnesium carbonate. In spite of these limitations, it was possible, by controlling exposure and minimizing time cycles, to extrude wet magnesia mixes containing ammonium alginate. Sodium alginate was also used since it is more stable in this chemical environment. The data listed in Table 16 were obtained within a few minutes after mixing. Ultrasonic effects noticeable were a reduction in pressure required, together with an increase in rate.

Table 16

EFFECT OF ULTRASONICS ON EXTRUSION OF FRESHLY PREPARED MIXES OF UNFUSED MAGNESIA WITH WATER AND AMMONIUM ALGINATE

Ultrasonic Activation of 3/8-in. Die: 20 kc/sec
Extrusion Ratio: 13.6

Composition					
MgO, w/o	H_2O, w/o	Ammonium Alginate, w/o	Compression Load, psi	Ultrasonic Power, watts	Extrusion Rate, in./min
75.4	23.0	1.6	7000	0	0
			2000	500	34
				1000	46
78.2	19.4	2.4	3000	0	125
			2000	0	0
				500	142
				1000	243
77.6	20.0	2.4*	2000	0	243
			1000	500	79
				1000	108

* Sodium alginate used in place of ammonium alginate.

E. Alumina, Porcelain, and Titania

As part of another program, samples of these ceramic materials, mixed with their respective binders, were extruded at water contents lower than normally considered extrudable. The 3/8-in. rod die with an extrusion ratio of 13.6 was utilized. The results are listed in Table 17. In each case, the data support the observations of lower pressure and higher extrusion rate, resulting from ultrasonic activation. Where comparisons were possible, the ultrasonically extruded shapes showed better surface finish and less die pickup. With these intentionally low moisture contents, only the ultrasonically extruded materials appeared satisfactory.

In addition, the titania mix containing 11.5 w/o water was also extruded using the 1/16-in. round die at an extrusion ratio of about 500. Significant extrusion took place only with ultrasonics at 10,000 psig pressure. The as-extruded rod was fragile because of its small diameter, but appeared suitable for further processing (Fig. 17).

F. Zirconia

Other ceramic materials studied in the work covered by this report were of particle sizes ranging upward from 1 µ. The work described here was done on stabilized zirconia formulations which are of considerably smaller particle-size distribution (well into the submicron region), and which, therefore, simulate very finely divided materials such as colloidal precipitated beryllia, alumina, or thoria. The plasticizer consisted of 4 w/o starch, 12 w/o glycerine, and varying quantities of water. The material was extruded on a 25-ton hydraulic press fitted with a 3/8-in. diameter die which was activated in the axial mode at 20 kc/sec.

The results (Table 18) show that the ultrasonic extrusion of zirconia formulations with water contents of 10.35 and 7.53 w/o can be accomplished with a greater than 30-fold rate increase at constant extrusion pressure, and a greater than 45% reduction in extrusion pressure at constant rate. It should be noted that the drier formulation could be extruded under ultrasonic die activation at the same rate and pressure as was required for the 10.35% water content material. Thus, a greater than 25% reduction in water content could be achieved, and an improved dimensional stability is expected from this lower water content.

Table 17

ULTRASONIC EXTRUSION OF VARIOUS CERAMIC MATERIALS

Axial Mode Die Activation: 20 kc/sec
Round Die: 3/8 in.
Extrusion Ratio: 13.6

Material	Binder	Water Content, w/o	Ultrasonic Power, watts	Extrusion: Pressure, psi	Extrusion: Rate, in./min	Extrusion: Condition
Alumina*	2% polyvinyl alcohol	12.0	1000	10,000	0	
			0	10,000	0	
		15.2	1000	2,000	163	Rod smooth
			0	4,800-10,000	80	Extrusion stopped
Porcelain**	2% polyvinyl-acetate	16.5	1000	10,000	87.5	
			0	10,000	0	
			1000	10,000	168	
		20.4	1000	2,000	243#	Surface clean and smooth
			0	2,600	243#	Appreciable die pickup
Alkaline TiO_2	2% polymeric	9.5	1000	10,000	53	Rod crumbled easily
			0	10,000	0	
			0	10,000	52	Rod crumbled easily
Acid TiO_2	2% polymeric	11.5	1000	4,000	243#	Extruded readily with smooth surface cracks visible
			0	6,000	243#	Surface cracks visible
			1000	1,800	243#	Smooth

* Alumina 614 ball-milled to a 30-m^2 surface area and approximately 1.5-μ average particle size (alumina 38900 has about 7-μ particle size and 15-m^2 surface area).

** Ball-milled.

\# Maximum extrusion rate of press.

Table 18

ULTRASONIC EXTRUSION OF ZIRCONIA*

20-kc/sec axial-mode excitation of 3/8-in. inner diameter rod-type die

Extrusion Ratio: 13.6

Water Content, w/o	Extrusion Load, psi	Extrusion Rate, in./min	Ultrasonic Power Input, watts	Dry Density**, g/cc
10.35	3000	7.2	0	2.53
		238	500	2.58
	3400	43.8	0	2.51
	2450	45	500	2.45
	1950	45.5	1000	2.52
7.53	3000	0	0	
		80	500	2.64
		232	1000	2.63
	3600	70	0	2.70***
	2400	76.2	1000	2.70***
	2000	75.0	1500	2.71***

* Stabilized ZrO_2 through courtesy of General Electric, Aircraft Nuclear Propulsion, Cincinnati, Ohio.

** Density determined by mercury displacement method; samples air-dried for 96 hr at ambient temperatures except for those marked ***.

*** Oven dried for 15 hr at 120°C.

IX. SUMMARY AND CONCLUSIONS

The application of ultrasonic energy appropriately applied to the die or container of laboratory or commercially available extrusion presses has been extended from early work in the extrusion of lead and aluminum to the cold extrusion of plasticized ceramic compositions with significant improvements in increased extrusion rate, decreased extrusion pressure, and in improved extruded specimen properties. It has also been found possible to extrude materials which are normally nonextrudable because of their low plasticizer or water content when ultrasonic activation of the extrusion array is carried out. It has been postulated that the ultrasonic effects observed are derived from reduction of surface friction, shear thinning of the thixotropic systems, particle orientation, surface-film rupture, and wetting phenomena.

1. Reduction of extrusion pressure appears to be a universal effect, since it was observed with every material and combination. Depending on other conditions, the reduction from parallel nonultrasonic controls varied in magnitude from 30% to nearly tenfold for the more nonplastic mixes. Extrusions which could not be started, or which stopped, could be initiated with ultrasonic application.

2. Increase in extrusion rate varied from a small factor (for compositions easily extruded without ultrasonics) to several hundredfold for the stiffer mixes. This effect was observed with all materials and mixes.

3. Extrusion of low plasticity ceramics has been demonstrated. An outstanding observation throughout this investigation was that ultrasonic die activation initiated and sustained satisfactory extrusion under conditions that gave no extrusion at all without ultrasonics. The obvious implication of this is that it should be possible to reduce the quantities of materials which are added to facilitate extrusion, but which are otherwise undesirable and must be removed in subsequent processing.

   Fused, ground alumina (38900) could be ultrasonically extruded with 15% less water than the minimum content without ultrasonics, and only 40-60% of that used in normal commercial practice. Significant improvement in the strength of as-extruded shapes resulted, as well as reduced shrinkage and deformation in drying and firing. Improvements in density, strength, and structural integrity of the vitrified shapes were observed, but exactly parallel firings are required for exact comparison between high and low water control specimens. The lower practical operating limit for moisture content can be reduced by ultrasonics, and a wider variety of liquids can be considered for extrusion vehicles.

   Reduction of binder and plasticizer content is an equally important advantage in ultrasonic extrusion. Compositions normally using 3 w/o ammonium alginate as a plasticizer can be extruded with 0.2 w/o plastizer when ultrasonically activated. Even low water content compositions can be processed with 1% ammonium alginate content.

4. Improved surface finish resulted from applying ultrasonics in all cases where a comparison could be made with a nonultrasonic extrusion. The improvement was evidenced by a smoother surface and freedom from cracks, tearing, and peeling. When steel dies were used, abrasion of the die surface sometimes caused a superficially discolored surface in nonultrasonic extrusions. The comparable ultrasonic extrusions showed little or no discoloration as the ultrasonic power level was increased.

5. Improved specimen properties after firing were observed in comparing like compositions with and without ultrasonic activation. Ultrasonically extruded specimens, which were fired in the same kiln loading as the corresponding controls, showed small but consistent increases in fired density. Water absorption was approximately 75% of the control. The highest moduli of rupture in the fired specimens were found in the ultrasonic specimens even though these required only 25% of the extrusion pressure of the controls. In future work, comparisons should be made between normal compositions and ultrasonically extruded, low-moisture-content compositions.

The apparatus configurations utilized in the earlier hot lead and aluminum extrusion investigations were readily extended and modified for work with ceramics. Further evolution of practical adaptation to commercial hydraulic and augur extruders has taken place incident to other programs. In the present work, the most effective activation site was found to be the extrusion die. Flexural activation of the container showed measurable effects, and might supplement die activation for difficult extrusions. Effective power levels for the specimen size and stiffness investigated appeared to be from 250 to 1500 watts, with an indication that stiffer mixes could be benefited at higher power levels. Extrusion equipment of larger size and input power has been successfully operated on other materials. Multiple transducer configurations permitted access to the die face; advanced designs are under consideration for improved access. No attempts were made to determine if optimal die design for ultrasonic extrusion was different from that for nonultrasonic extrusion. The aforementioned effects were observed in the ultrasonic activation of dies to produce 3/8-in. rod, hexagonal rod, hollow hexagonal tubing, ribbon, and 1/16-in. diameter rod. Extrusion ratios from 13.6 to 500 appear to be practical.

Ultrasonic extrusion of plasticized powders appears to be generally applicable in that a wide range of powders and plasticizers has been studied in this work. The particle size was from the submicron zirconia to the 100-μ tabular alumina. Fused oxides (such as 38900 alumina), nonsintered polishing grade alumina, Ajax P clay, chemically reactive magnesia, porcelain, and titania all show an appreciable ultrasonic extrusion effect. These compositions were plasticized with alginates, starch-glycerin, and several polymers.

The apparent universality of these effects suggests their application to other materials of interest in nuclear engineering, such as the oxides and carbides of uranium and thorium, beryllia, graphite, and cermet mixtures including those incompatible with aqueous vehicles. With proper application, ultrasonic extrusion may become a practical means for fabrication of materials not previously successfully extruded.

Possibilities for coextrusion are offered by the ultrasonic control of plasticity. One of the difficulties in simultaneous coextrusion, is maintaining the correct stiffness match between the two mixes. By applying controlled ultrasonic power to one of the materials, it should be possible to coextrude mixes which normally would require different conditions.

APPENDIX

PROPERTIES OF CERAMICS

APPENDIX

PROPERTIES OF CERAMICS

Selected physical properties and composition are listed for ceramics used in this investigation. Properties shown in Table A-I include: (a) particle size distributions, determined by the MSA-Whitby Analyzer technique (29); (b) density measured by American Ceramic Society standard method for true specific gravity (30); and (c) moisture loss, determined by heating samples to 800°F for 2 hr. Figure A-1 depicts particle size distributions for the ceramics studied; photomicrographs of the ceramics are given in reference 31.

Table A-1

PROPERTIES AND COMPOSITION OF CERAMICS

Norton Alumina, E-111-H: nonreacted, abrasive;
38900: precalcined, refractory

IMC-U99* Magnesia, granular

	E-111-H	38900	U-99 Magnesia
	Composition, w/o		
Al_2O_3	99.01	99.90	--
SiO_2	0.98	0.04	0.05
MgO	--	--	99.50
Fe_2O_3	.11	.01	0.07
TiO_2	.05	--	
Na_2O	0.75	0.05	
CaO	--	--	0.05
Other	--	--	0.03
Crystal Density, g/cc	3.791	3.95	--
Moisture Loss, w/o	0.629	0.085	--

Particle Size Distribution, %

Size Range, μ	E-111-H	38900 Batch 1	38900 Batch 2	38900 Special Grind	U-99 Magnesia
0-1.5	23.3	2.9	1.8	14.8	5.2
1.5-3.0	21.3	16.6	8.0	16.1	12.4
3.0-6.0	16.4	24.9	42.2	30.4	11.7
6.0-9.0	14.9	22.7	39.7	22.8	29.5
9.0-15.0	13.4	12.7	6.7	12.4	24.7
15.0-20.0	6.9	3.2		0.7	12.9
20.0-25.0	2.5	1.5		0.7	2.8
25.0-30.0	1.0	1.5			0.7
Mean Diameter, μ	2.81	4.90	4.70	4.00	8.25

* International Minerals and Chemical Corporation.

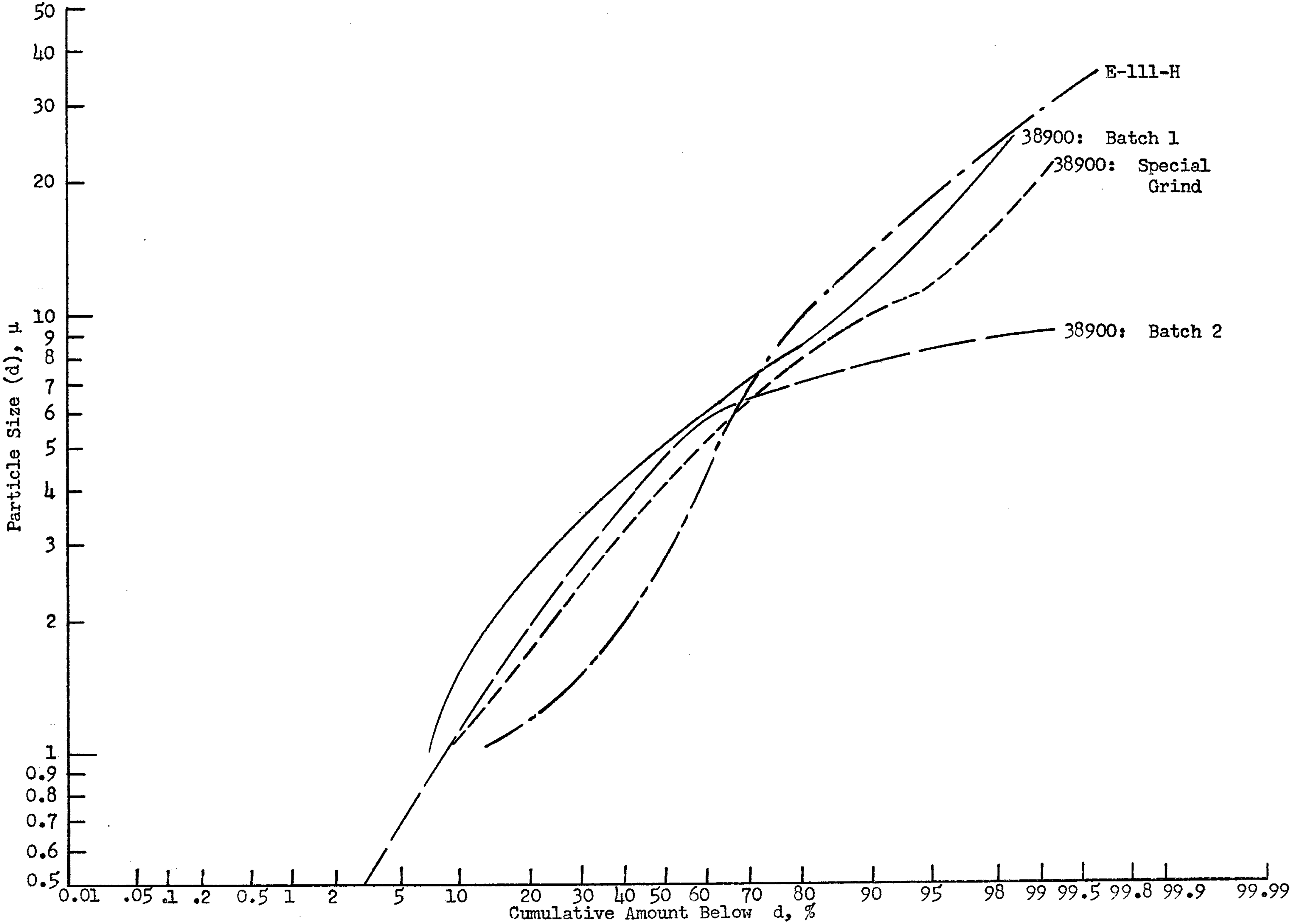


Fig. A-1: PARTICLE SIZE DISTRIBUTION OF ALUMINAS

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